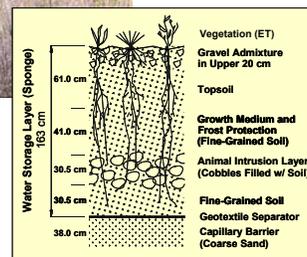


Enhancements to Natural Attenuation: Selected Case Studies



May 2007

Washington Savannah River Company
Savannah River Site
Aiken, SC 29808

Prepared for the U.S. Department of Energy
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SRNL
SAVANNAH RIVER NATIONAL LABORATORY

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Photos on cover: Upper left – Constructed Wetland in northern California (obtained from University of Montana website on constructed wetlands). Upper right – Continuous trencher used in permeable reactive barrier construction, Coast Guard Site, Elizabeth City, NC (obtained from Clu-In internet training slide package). Bottom - photo and cross-section - Monticello, Utah, CERCLA Disposal Cell: Evapotranspiration Cover with Capillary Barrier (provided by Jody Waugh).

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Enhancements to Natural Attenuation: Selected Case Studies

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Acronyms

ACAP	Alternative Cover Assessment Project
AFB	Air Force Base
AFCEE	Air Force Center for Environmental Excellence
bgs	below ground surface
CERCLA	Comprehensive Environmental Response, Compensation and Liability Act
CMT	continuous multi-channel tubing
CSL	compacted soil layer
cVOCs	chlorinated volatile organic contaminants
DNAPL	Dense non-aqueous phase liquid
DOE	Department of Energy
EA	Enhanced Attenuation
EISB	Enhanced <i>in situ</i> Bioremediation
EPA	Environmental Protection Agency
ERP	Environmental Remediation Program
ESB	Engineering Support Building
ET	evapotranspiration
FRTR	Federal Remediation Technology Roundtable
ITRC	Interstate Technology Regulatory Council
LCU	semi-confining clay unit
LSU	lower sand unit
MFGU	middle fine-grained unit
MNA	Monitored Natural Attenuation
NASA	National Aeronautics and Space Administration
NPDES	National Pollutant Discharge Elimination System
OD	outside diameter
ORNL	Oak Ridge National Laboratory
OSWER	Office of Solid Waste and Emergency Response
P	precipitation
PET	potential evapotranspiration
PID	photoionization detector
PLFA	phospholipid fatty acids
PRB	permeable reactive barrier
PTA	primary treatment area
RCRA	Resource Conservation and Recovery Act
RFI	RCRA Facility Investigation
S_c	mean soil water storage capacity
S_p	peak soil water storage capacity
SITE	Superfund Innovative Technology Evaluation
SWCC	soil water characteristic curves
TDR	time domain reflectometry
TIR	Thermal Infrared Imaging
USCG-SC	United States Coast Guard Support Center
USEPA	United States Environmental Protection Agency
USGS	United States Geological Survey
USU	upper sand unit
VFA	volatile fatty acid
WAG	Waste Area Group
ZVI	zero valent iron

Chemicals

Cr	chromium
CF	chloroform
CH ₄	methane
cis-DCE	cis-1,2-dichloroethene
CO ₂	carbon dioxide
CT	carbon tetrachloride
DO	dissolved oxygen
HCA	hexachloroethane
MeCl	methylene chloride
PCA	pentachloroethane
PCE	tetrachloroethene
TCE	trichloroethene
TeCA	1,1,2,2-tetrachloroethane
VC	vinyl chloride

1.0 INTRODUCTION

In 2003 the US Department of Energy (DOE) embarked on a project to explore an innovative approach to remediation of subsurface contaminant plumes that focused on introducing mechanisms for augmenting natural attenuation to achieve site closure. Termed enhanced attenuation (EA), this approach has drawn its inspiration from the concept of monitored natural attenuation (MNA).

MNA is an approach where the cumulative impact of natural attenuation processes (i.e. the natural attenuation capacity) is sufficiently large to yield a stable or shrinking plume within a reasonable period of time in comparison to application of more active forms of plume management. MNA is recognized as a viable plume management approach by the US Environmental Protection Agency (EPA), one that is codified in a protocol (EPA, 1998) and OSWER directive (EPA, 1999). The directive describes the attenuation processes of MNA in the following manner:

The ‘natural attenuation processes’ that are at work in such a remediation approach include a variety of physical, chemical, or biological processes that, under favorable conditions, act without human intervention to reduce mass, toxicity, mobility, volume, or concentration of contaminants in soil or groundwater. (EPA, 1999; pg. 3)

This directive also includes the following statements:

- *“EPA prefers those processes that degrade or destroy contaminants.” (pg. 3)*
- *“EPA expects that source control and long-term performance monitoring will be fundamental components of any MNA remedy.” (pg. 3)*
- *“While MNA is often dubbed ‘passive’ remediation..., its use at a site does not preclude the use of ‘active’ remediation...” (pg. 4)*
- *“...by definition, a remedy that includes the introduction of an enhancer of any type is no longer considered to be ‘natural’ attenuation.” (pg. 4)*

Following the EPA protocol for MNA, sites can be evaluated to determine if this approach is justifiable. According to information reported in EPA (2004) for remedial actions at 1062 National Priority List sites between 1982 and 2002, MNA was included as the sole or partial remedy at 201 sites (19% of the total). This statistic illustrates the importance of natural attenuation processes in recent site remediation decisions. However, there are many sites for which the natural attenuation capacity of a system is insufficient for traditional MNA to apply. It is within this context that DOE began to explore EA. Specifically, the following question is posed: “Are there passive, sustainable enhancements that can be introduced to a subsurface plume system to augment natural attenuation processes to increase the attenuation capacity of the system sufficiently to achieve regulatory objectives?” To place some limits on the scope of this project, DOE chose to focus on chlorinated volatile organic compounds (cVOCs) such as tetrachloroethene (PCE) and trichloroethene (TCE) because they are a major source of contamination at most DOE sites and are recognized as among the major contaminants at Superfund sites across the US.

In a report developed as part of the EA project, there was an attempt to explore the spectrum of possible enhancements that might become part of a comprehensive plume management strategy (Early, et al., 2006). These enhancements covered a broad range of approaches and are summarized in Figure 1. Potential enhancements range from engineering approaches (e.g. french drains, slurry walls, etc.) that have been used for decades and extensively tested, through more contemporary technologies that still have a relatively long deployment record (e.g. permeable reactive barriers (PRBs), alternative designs for engineered covers), to innovative approaches that are the subject of current research and development (e.g. diffusion barriers with vegetable oil, bioaugmentation). However, most potential enhancements involve technologies that are familiar to environmental engineers and regulators. This is advantageous

because their relative maturity and the existing knowledge base for their performance under a variety of site conditions generally impart a heightened level of confidence that their expected performance is somewhat predictable once deployed (i.e. lower risk of failure).

The natural attenuation mechanisms considered for MNA tend to focus on processes occurring and having their greatest impact within the main body of a plume (e.g. advective dispersion, biodegradation). In contrast, as noted in Figure 1, some enhancements for EA are designed for deployment in source zones. These enhancements function to reduce the source loading to a plume by reducing infiltration or decreasing the flow of groundwater through a source or by enhancing further degradation of residual source contaminants remaining after active source treatment has concluded. A reduction in the source term also can help facilitate developing a stable or shrinking plume.

As noted above, one of the key criteria for enhancements is that they must be sustainable. That is, they must operate with sufficient efficiency to reduce contaminant flux to maintain a shrinking plume until such time that purely natural processes at the site can assume the full burden for attenuation. Obviously, this is an important constraint and limits the type of enhancements that can be selected for an EA remedy; those requiring frequent post-deployment intervention generally will not be acceptable. However, a major challenge to technology developers and remediation specialists is the ability to define or predict the sustainability of an enhancement. In general, this will be determined by site-specific factors and is not well-constrained by current information. At present, many potential enhancements have not been subject to long-term testing and careful monitoring to assess and predict their sustainability. For example, french drains are generally acknowledged to be a robust engineering approach that are known to operate effectively for decades in many settings. Likewise, engineered covers have been used for many years in an attempt to hydraulically isolate buried waste landfills even though they are known to fail eventually for a variety of reasons. In contrast, the performance record for PRBs is considerably shorter (10-15 yrs), although a multi-agency investigation has addressed this issue (FRTR, 2002). Other more innovative potential enhancements (e.g. bioaugmentation), while very promising, currently are under development and testing and may only have several years of field data and few full-scale applications. To a large extent, the success of EA as a remediation strategy will depend upon obtaining critical information on sustainability for enhancements.

A closely related concern for some potential enhancements is the question regarding how passive they will be following deployment. For example, this is a particular concern for some chemical and biological attenuation mechanisms where injection of amendments is used to initiate the process. Can biostimulation, bioaugmentation, or abiotic enhancements be sustained without periodic injection of nutrients?

At this stage of development of the EA approach for plume management it is not possible to resolve all of the questions related to sustainability, cost-effectiveness, and regulatory acceptance of potential enhancements. Rather, they are cited as issues to be addressed by ongoing and future investigations.

EA not only involves application of enhancements to achieve regulatory objectives, but also requires that a firm theoretical and practical (i.e. monitoring) basis exists for verifying that a condition of mass balance of contaminants exists in the source-plume system. While critical to the overall success of EA, the case studies presented in this document focus on examples where selected enhancements have been implemented with information related to their performance. However, they do not attempt to address the equally important issues of evaluating the rates of individual attenuation mechanisms, measuring the natural attenuation capacity of the system, or development of practical strategies for long-term monitoring.

1.1 POTENTIAL ENHANCEMENTS

Sections 2 to 5 of this document present a sequence of six case studies of potential enhancements that might have application in EA for many sites. The technology approaches include the following:

Engineered covers (Section 2)

- Alternative covers: Enhanced soil water storage and evapotranspiration in the source zone by C.H. Albright, W.J. Waugh, and C.H. Benson
- The impact of a RCRA-type engineered cover at an ORNL burial ground by T.O. Early and P.M. Jardine

Biostimulation/bioaugmentation of a DNAPL source (Section 3)

- Enhancing the Dechlorinating Capabilities of Indigenous Microbial Consortia through Bioaugmentation by Eric D. Hood, David E. Major

Permeable reactive barriers (Section 4)

- Conventional PRB using Zero-Valent Iron (ZVI) by O.R. West and R. Wilkin
- Full-Scale Mulch Biowall at Offutt Air Force Base (AFB), Nebraska by T.O. Early and Erica Becvar

Constructed wetland at a DoD site (Section 5)

- Wetland Enhancement-Reactive Mat at the Aberdeen Proving Ground-West Bank Canal Creek by Gary Wein, Michelle Lorah, and Emily Majche

These examples are intended to cover a range of applications involving enhancements to the source zone (covers, biostimulation/bioaugmentation), the main body of a dissolved plume (PRBs), and treatment at the discharge zone (constructed wetland). Likewise, the nature of the attenuation process varies from a physical attenuation mechanism (i.e. limiting infiltration with covers), primarily abiotic degradation (PRBs with ZVI), and biodegradation processes (PRB with a mulch biowall, constructed wetland, and biostimulation/bioaugmentation). The enhancements favor those leading to destruction of contaminants, a condition favored by EPA in the MNA guidance (EPA, 1999). The examples were not chosen because they are clear successes in terms of enhancement efficiency or have proven sustainability. Rather, the case studies point out potential concerns with the respective technologies and the post-deployment monitoring period for most of them is too short to objectively assess their sustainability. These concerns and limitations emphasize the continuing need to perform targeted field testing and to accumulate longer-term monitoring data to evaluate their longevity.

1.2 ORGANIZATION OF CASE STUDIES

The discussion on alternative cover designs (Section 2) is unique among the six case studies that follow. Rather than focusing upon a single site and measures of performance of the cover in reducing source loading to a contaminant plume, this summary evaluates the effectiveness of covers across the spectrum of climatic conditions in reducing infiltration of precipitation. As such, it provides a framework for understanding the important elements of cover design in different climate regimes.

The other five case studies address specific examples of enhancements from which performance objectives such as sustainability and reducing mass flux are evaluated. These investigations encompass the following general topic areas:

- Site description (location, history, geology, hydrology, and nature and extent of contamination)

- Application of an enhancement (type, objectives, construction details, etc.)
- Impact of enhancement on measurable properties
- Information on the sustainability of the enhancement
- Summary and conclusions

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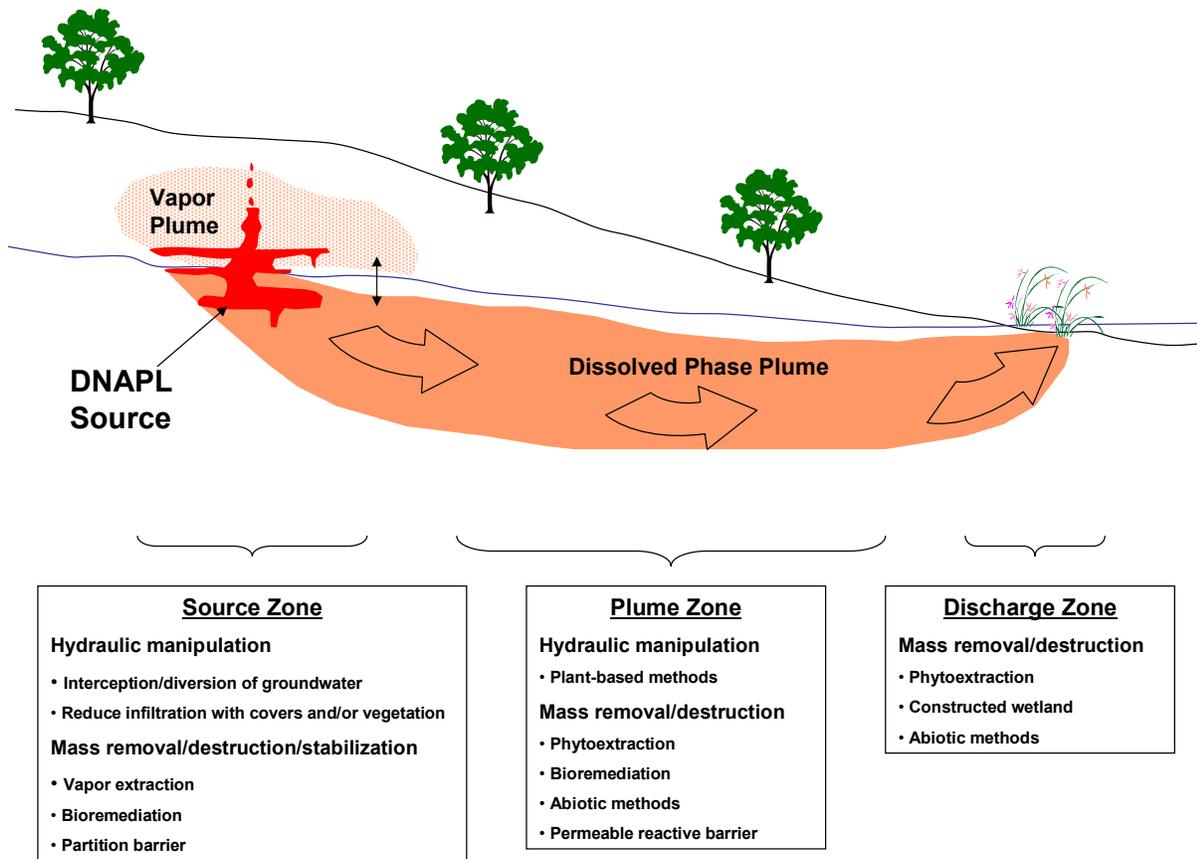


Figure 1. Examples of enhancements to natural attenuation that might be applicable at various locations within a cVOC plume.

2.0 ENGINEERED COVERS

Introduction:

Engineered covers of various designs have been used for many years as a containment strategy for landfills and buried waste sites in an effort to limit the amount of infiltration penetrating to the waste and mobilizing contaminants. Use of a simple compacted clay layer or asphalt cap in early covers has given way more recently to multi-layer designs incorporating geofabric, capillary barrier, and vegetative cover elements. Within the context of EA, source containment through application of engineered covers is a means of reducing the mass flux of contaminants feeding a dissolved phase plume. Many concerns regarding the longevity and design of these covers have been raised including the gradual deterioration of the effectiveness of cover layers leading to increased rates of infiltration over time. In addition, how to design effective covers appropriate to a variety of climatic conditions has been a continuing issue for the technical community.

In 1998 EPA initiated an extensive project to evaluate alternative cover designs in a series of demonstrations in different climatic regimes located across the US. The objective of this effort has been to develop design strategies that result in sustainable cover performance by working with nature rather than trying to overcome it. The first case study summarizes the results of this project at 11 sites ranging in climate from arid to humid. Evaluation methods focus on different design elements and the effectiveness of the covers in reducing infiltration. Performance results for reduction of infiltration associated with alternative covers in humid areas indicate reduced effectiveness in comparison to covers in drier climates.

A recent specific example is presented as the second case study and involves application of a RCRA multi-layer cover at an inactive waste burial site at Oak Ridge National Laboratory (ORNL) in Tennessee. The effectiveness of the cover is examined by evaluating changes in hydrology and integrated discharge of tritium contamination mobilized from the burial ground. In this example, significant reduction of tritium flux apparently was related to deployment of the cover, but the post-deployment time interval for observation is very short (~6 mo.) and long-term sustainability of the cover performance is uncertain.

Alternative Covers: Enhanced Soil Water Storage and Evapotranspiration in the Source Zone

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INTRODUCTION

Reliance on natural processes to clean up contamination, referred to as Monitored Natural Attenuation (MNA), has increased in response to greater awareness of the limitations of engineered remedies for achieving ground water and soil remediation goals (EPA 1999, NRC 2000). Conversely, the capacity of natural processes alone may not be adequate to attain remediation goals in a timely manner. Enhanced Attenuation (EA) is a strategy that bridges the gap between active, engineered solutions and passive MNA (ITRC, 2006). EA involves human intervention to enhance or accelerate natural processes. Successful enhancements should increase the magnitude of natural attenuation processes beyond what would occur without intervention (Early *et al.* 2006). A successful enhancement is also a sustainable manipulation; i.e., continuous, long-term intervention is not required. Hence, spanning the gamut of remediation options and philosophies, EA could be viewed either as help for Mother Nature or as sustainable engineering. EA applications also target different portions of the plume trail, from inhibiting contaminant loading at the source to augmenting natural processes down gradient.

This case study targets contaminant loading at the source and approaches the EA concept from the perspective of *sustainable engineering*. Loading—movement of contaminants from the source to the plume—is the product of concentration and flow (Early *et al.* 2006). This case study addresses the flow component of source loading; specifically, the use of engineered earthen covers or caps to slow infiltration and percolation of rainwater through the source zone. Many conventional engineered covers, designed for solid and hazardous waste landfills, rely on the low hydraulic conductivity of a compacted soil layer to limit infiltration and percolation. An alternative approach is to manipulate the soil water balance of a source zone by enhancing soil water storage and evapotranspiration. The performance of an alternative cover depends upon the climatology, soil hydrology, and plant ecology of the site.

This study compares the hydrologic performance of alternative covers over a range of climates, soil types, and vegetation types. The first section of the paper briefly reviews underlying concepts and experience with both conventional and alternative cover designs. The greater part of the paper, a comparison of alternative covers tested in different climatic settings, is based entirely on water balance data from large-scale lysimeters or test sections constructed under EPA's Alternative Cover Assessment Project (ACAP) (Albright *et al.* 2004). The last section draws conclusions from the ACAP comparisons, and then recommends follow-up work on near-term processes that can change cover performance, an approach for projecting long-term performance, and an approach to improve the sustainability of existing conventional covers.

CONVENTIONAL AND ALTERNATIVE COVERS

Most conventional cover designs include compacted soil layers (CSLs) to impede percolation through underlying contaminated materials (EPA 1989, DOE 1989). Although design targets and performance standards for CSLs vary, typically, the goal is a saturated hydraulic conductivity of less than 1×10^{-7} cm/s. Multiple lines of evidence, including EPA and DOE field studies, laboratory studies, and monitoring data, show that many existing CSLs fall short of the low-hydraulic conductivity targets, often at the time of or shortly after construction, and sometimes by several orders of magnitude (Daniel 1994, Melchoir 1997, Benson et al. 1999a, Benson 1999, Benson 2001, Albrecht and Benson 2001, Albright et al. 2004). Several reasons are cited:

- Unanticipated ecological consequences of designs that encourage biointrusion (Hakonson 1986, 1992, Suter *et al.* 1993, Bowerman and Redente 1998, Waugh *et al.* 1999, Waugh 2004).
- Compaction either dry or wet of optimum during construction (Daniel 1994, Benson *et al.* 1999a).
- Desiccation cracking (Boyton and Daniel 1984, Daniel 1994, Albrecht and Benson 2001).
- Differences between laboratory and field-determined hydraulic conductivities (Daniel 1984, Rogowshi 1990, Benson *et al.* 1999a).
- Freeze-thaw cracking (Kim and Daniel 1992, Benson and Othman 1993).
- Differential settlement (Jessberger and Stone 1991, LaGatta 1992, Daniel 1994).
- Retention of borrow soil structure (clods) during construction and pedogenesis (soil development processes) after construction (Benson and Daniel 1990, Benson 1999, 2001, Albright *et al.* 2004, Waugh 2004).

Advances in the science of cover performance, and lessons learned from monitoring conventional covers, contributed to the development of alternatives to the low-hydraulic conductivity designs. In many arid and semiarid ecosystems, relatively low precipitation, high potential evapotranspiration (ET), and thick unsaturated soils limit recharge (Gee and Tyler, 1994). Alternative covers that mimic this natural water conservation may provide long-term hydrologic isolation of subsurface contaminants (Clarke *et al.* 2004). Alternative covers generally consist of thick, finer-textured soil layers that store precipitation in the root zone where it can be removed seasonally by ET (Anderson *et al.* 1993). Capillary barriers consisting of coarse-textured sand and gravel placed below this soil “sponge” can enhance water storage and limit unsaturated flow (Nyhan *et al.* 1990, Ward and Gee 1997).

The sustainability of alternative covers relies, in part, on the establishment and resilience of a diverse plant community. Changes in the plant community inhabiting a cover will influence soil water movement, ET rates, and the water balance of a cover. However, plant community dynamics are complicated and effects are difficult to predict. Even in the absence of large-scale disturbances, seasonal and yearly variability in precipitation and temperature will cause changes in species abundance, diversity, biomass production, and soil water extraction rates on covers (Anderson et al. 1993, Link *et al.* 1994). Investigations of natural analogs can provide insights as to how ecological processes may influence the sustainability of alternative covers (Waugh *et al.* 1994). Evidence from natural analogs can improve our understanding of vegetation responses to climate change and disturbances; effects of vegetation dynamics on ET, soil hydraulic conductivity, soil erosion, and animal burrowing; and effects of soil development processes on water storage, hydraulic conductivity, and site ecology.

PERFORMANCE OF ALTERNATIVE COVERS

Site Descriptions

The ACAP field program consisted of 11 sites located in seven states so as to represent a broad range of climates, soil types, and vegetation types (Albright *et al.* 2004). Locations of the field sites are shown in Figure 1 and a summary of cover types and climate characteristics is given in Table 1. Using the ratio of

precipitation (P) to potential evapotranspiration (PET) to define climatic zones (UNESCO (1979)), one site has an arid climate ($0.03 < P/PET \leq 0.2$), 6 sites have a semi-arid climate ($0.2 < P/PET \leq 0.5$), 1 site has a sub-humid climate ($0.5 < P/PET \leq 0.75$), and 3 have a humid climate ($P/PET > 0.75$). The average annual precipitation ranges from 119 (Apple Valley, CA) to 1263 mm (Albany, GA). Snowfall is appreciable at 5 sites (Helena and Polson, MT; Omaha, NE; Cedar Rapids, IA; Monticello, UT). The maximum average monthly high temperature ranges from 22 °C (Marina, CA) to 37 °C (Apple Valley, CA), and the minimum average monthly low temperature ranges from -11 °C (Helena, MT and Omaha, NE) to 8 °C (Albany, GA).

Cover Designs

The profiles of the 14 alternative covers evaluated are shown in Figure 2. Eight of the alternative covers were monolithic covers (i.e., a thick layer of finer textured soil overlain by topsoil) and 6 were capillary barriers. All of the capillary barrier designs consisted of two layers, a fine-textured soil layer overlying a coarse layer. The primary purpose of the capillary break was to enhance the storage capacity of the overlying finer-textured layer. The test sections were sloped at 5 or 25%, depending on the predominant condition at each site (Table 1). Construction of all but one of the ACAP test sections was completed by Fall 2000 (Apple Valley, CA was a late addition to the program, and was constructed in March 2002). A detailed description of the construction of each test section can be found in Bolen *et al.* (2001) and Roesler *et al.* (2002) (both available at www.acap.dri.edu, May 2004).

All covers were constructed with local soils and all of the test sections were constructed with methods and procedures typical of engineering practice for construction of landfill covers. Full-scale construction equipment was used to place and compact soils. An extensive sampling program was conducted during construction of the covers to thoroughly characterize all soils used.

The vegetation used at each site is summarized in Table 2. All of the sites were seeded with a mixture of annual and perennial grasses. Three of the sites (Apple Valley, CA; Monticello, UT; Polson, MT) also included shrubs, and at two sites (Albany, GA; Cedar Rapids, IA), hybrid poplar trees were transplanted and an understory of grasses was seeded.

Materials and Methods

Lysimeters

A key feature of all ACAP test sections was a large (10 m × 20 m), instrumented, pan-type lysimeter (Figure 3) used for direct measurement of surface runoff, soil water storage, and percolation from a full-depth cover profile. The base and sidewalls of each lysimeter consisted of a low-density polyethylene geomembrane. The geomembrane was overlain with a geocomposite drainage layer for protection and to transmit water from the base of the cover profile to a collection and measurement system. Diversion berms on the surface were used to prevent run-on and collect run-off as well as to delineate the edges of the lysimeter. Cover profiles were constructed with buffer areas at least 3 m wide around the perimeters of the lysimeters to reduce boundary effects and to provide areas for annual sampling of soil and vegetation. Methods used to install the lysimeters are described in Benson *et al.* (1999b).

An extensive sampling program was conducted during construction to characterize the in-place cover soils. Four disturbed samples (20-L buckets) and four undisturbed samples were collected from each lift of soil immediately after placement. Two of the undisturbed samples were collected through the entire lift using thin-wall sampling tubes (76 mm diameter), and two were collected as hand-carved blocks (200 mm diameter and length). The disturbed samples were analyzed for particle size distribution (ASTM D 422), Atterberg limits (ASTM D 4318), organic matter content (ASTM D 2974), and compaction behavior

(ASTM D 698). The undisturbed samples were tested to determine saturated hydraulic conductivities (ASTM D 5084 or D 5856) and soil water characteristic curves (SWCC) (ASTM D 6836). Results of all of the tests are contained in Gurdal *et al.* (2003).

Soil water storage capacities (median, upper bound, and lower bound) for the alternative covers are summarized in Table 2. Soil water storage capacities were computed using the SWCCs from the samples collected during construction. For the monolithic alternative covers, the storage capacity was computed as the product of field capacity (water content at 33 kPa soil water matric potential) and thickness. This calculation of storage represents the maximum water storage in the soil profile rather than available water storage capacity (the difference between field capacity and wilting point), a parameter commonly used during cover design. Soil water storage capacity of the capillary barriers was computed using the method in Khire *et al.* (2000), which accounts for the additional storage in an overlying finer layer provided by the textural contrast at the capillary break. Storage capacities were computed for each SWCC.

Prior to construction of a cover profile in a lysimeter, a layer of soil simulating the existing source-zone soil was placed between the geocomposite drainage layer and the cover profile to replicate field conditions as closely as practical. The thickness of this layer varied between 150 mm and 600 mm. A root barrier (a non-woven geotextile studded with nodules containing trifluralin, a root inhibitor) was placed between the source-zone soil and cover soil layers to prevent root intrusion into the geocomposite drainage layer and the underlying percolation collection system. The extra soil layer and the root barrier were included to allay concerns associated with use of drainage lysimeters: (i) placement of the lysimeter geomembrane and overlying geocomposite drainage layer increases the water storage capacity in the soils above the lysimeter by creation of a capillary break at the soil-geocomposite interface, and (ii) transpiration by roots of the additional water held in storage by the capillary break.

In the ACAP lysimeters, the occurrence of percolation required some additional water to pass through the final cover into the underlying interim soils to bring the interim soils to field capacity and initiate percolation. Most of the ACAP lysimeters did record some percolation and, while percolation may have been delayed, the measured percolation rate was representative once percolation was initiated. The root barrier prevents plants from having access to water retained in the interim soil layer that may otherwise become deep percolation. Exclusion of roots from this layer minimizes transpiration of the artificially stored water and defines the root zone. Inclusion of the root barrier probably resulted in less water being transpired than might occur in an actual cover, where roots can grow through the interim cover and possibly into the waste.

Data Collection

Percolation and surface runoff were routed by pipes to basins equipped with instrumentation (pressure transducer, tipping bucket, and float switch) capable of measuring flows with a precision better than 1 mm/yr. A discussion of the flow measurement system and its precision can be found in Benson *et al.* (2001).

Soil water content was measured by vertical arrays of time domain reflectometry (TDR) probes in three nests located at the quarter points along the downslope centerline of each test section (Figure 3). Soil water storage was determined by integration of the point water-content measurements.

Meteorological parameters (precipitation, air temperature, relative humidity, solar radiation, wind speed, and wind direction) were also measured at weather stations placed in the buffer areas.

Results and Discussion

Results for the ACAP alternative covers are shown in Table 3. Performance of the covers in arid/semi-arid/sub-humid locations and humid locations is summarized followed by examples of cover performance at selected sites.

Cover Performance in Arid, Semi-Arid, and Sub-Humid Climates

Very low average percolation rates (< 2.0 mm/yr) were recorded for 7 of the 10 alternative covers located at the arid/semi-arid/sub-humid sites. Total percolation of less than 1.0 mm was transmitted from 6 of the 10 covers throughout the monitoring period. Average annual percolation rates greater than 10 mm/yr were recorded at semi-arid Altamont (14 mm/yr), through one of the covers at Sacramento (35 mm/yr) and at coastal Marina (61 mm/yr).

The cover at Helena, MT demonstrated excellent performance over the monitoring period and is shown as an example in Figure 4. Precipitation and low transpiration rates during the cooler months resulted in annual increases in soil water storage. Higher rates of evapotranspiration during the summer months consistently reduced water stored in the cover soils and resulted in only a trace amount of percolation during the field study.

The large amounts of percolation transmitted from the alternative covers in Sacramento, Altamont, and Marina were not anticipated. The variable performance at Sacramento and Altamont appears to be a response to annual variations in the transpiration capacity of the vegetation. For example, Figure 5 shows large variation in the amount of water removed each summer from the cover soils by the vegetation at Sacramento. Percolation occurred following a summer when insufficient water was removed by evapotranspiration and winter precipitation exceeded the soil storage capacity. In other years, vegetation reduced the water stored in the cover to sufficient levels limiting percolation the following winter.

At Marina, the water storage capacity of the cover soil was insufficient to store infiltration that occurred during wet seasons, resulting in the annual occurrence of water contents exceeding the storage capacity and hence, relatively high percolation rates (Figure 6).

Cover Performance in Humid Climates

Alternative covers at the humid sites (Albany GA, Omaha NE, Cedar Rapids IA) transmitted the most percolation of all covers tested. Average percolation rates ranged between 33.3 mm/yr (6.1% of precipitation) for the thicker capillary barrier in Omaha, NE and 159.6 mm/yr (18.4% of precipitation) for the monolithic cover in Cedar Rapids, IA. Some of the alternative covers in humid climates behaved in accordance with water balance principles (i.e., percolation was transmitted when the storage capacity was exceeded). For example, nearly all of the percolation transmitted by the two capillary barriers at Omaha, NB occurred when the soil water storage exceeded the calculated storage capacity during intense spring rainfalls.

In contrast, performance of the Albany, GA monolithic cover appeared to be independent of soil water status. Three distinct hydrologic periods are evident (Figure 7) in the data: (i) an initial 6-month period characterized by high percolation rates and high soil water storage prior to the development of the vegetation, (ii) a 21-month period of little percolation characterized by rapid development of the vegetation and drying of the soil profile in response to transpiration, and (iii) a final period, initiated by extensive drying of the soil profile in response to drought and transpiration when percolation rates were equal to those recorded during the first 6 months. During the third period, percolation followed soon after precipitation events, suggesting that desiccation cracks or root channels penetrated through the entire cover during the previous drying period.

Importance of Soil Water Storage

As a way to evaluate the effect of soil water for all sites, a comparison was made between the annual percolation rate and the ratio of peak annual soil water storage (S_p) to the mean soil water storage capacity (S_c). This comparison is shown in Figure 8. All of the sites where $S_p/S_c \leq 0.7$ (vertical line in Figure 8) have annual percolation rates less than 1.5 mm/yr. The data from the monolithic cover in Albany, GA are an exception, because percolation at this site was likely dominated by preferential flow for much of the experimental period. This threshold can be used as a conservative measure of the effective storage capacity of alternative cover soils (i.e., 70% of the storage capacity computed from the SWCC). However, at some sites this criterion may result in over design because many of the sites with $S_p/S_c > 0.7$ had percolation rates less than 1.5 mm/yr.

The alternative covers in humid climates appeared ineffective in achieving low percolation rates. Average percolation rates between 81 and 144 mm/yr (10 to 15% of precipitation) were recorded for the monolithic covers with trees (Albany and Cedar Rapids), the two capillary barriers with grasses at Omaha transmitted percolation at rates ranging between 22 and 45 mm/yr (4.6 to 9.4% of precipitation). In contrast, with some exceptions, the alternative covers in the arid/semi-arid/sub-humid sites were generally effective with percolation rates less than 2.0 mm/yr (0.4% of precipitation).

The data from three sites in California (Sacramento, Altamont, and Marina) indicate that alternative covers do not always perform as expected. Relatively high percolation rates at these sites appear to be related to inadequate transpiration capacity and storage capacity. These unexpected conditions illustrate the need to carefully examine the attributes of vegetation and the storage capacity of cover soils. Analysis of the data from the ACAP sites suggests that the storage effective capacity in the field can be conservatively estimated as 70% of the storage capacity that is computed based on soil water characteristic curves measured in the laboratory.

CONCLUSIONS AND RECOMMENDATIONS

This case study evaluated an EA approach to slow percolation and contaminant loading by increasing soil water storage and evapotranspiration in the source area of a plume. A goal of enhancing the soil water balance, as an alternative to conventional engineered covers that rely on the low hydraulic conductivity of a highly compacted soil, is to accommodate ecological and soil development processes and thereby increase sustainability.

The soil water balance of several alternative covers representing a range of climatic conditions was evaluated using large lysimeters. For alternative covers constructed in humid climates with vegetation types varying from perennial grasses to hybrid poplars, rainfall seasonally exceeded soil water storage capacity causing percolation rates equivalent to between 5 and 15% of precipitation. This much percolation would likely be considered unacceptable for an engineered cover on a landfill. However, from the perspective of enhance attenuation, such covers may be adequate to reduce source loading of contaminants to the plume enough for attenuation processes in the plume to create a favorable mass balance and achieve remediation goals.

With some unexpected exceptions, alternative covers were very effective in limiting percolation at sites in arid, semi-arid, and sub-humid climates. In general, for covers with a ratio of the peak annual water storage to mean water storage capacity of ≤ 0.7 , percolation rates were less than 2.0 mm/yr (less than 0.4 % of precipitation). The exceptions illustrate the need to understand effects of plant community dynamics on transpiration, and soil development processes on water storage capacity and preferential flow. An ongoing study is evaluating soil hydraulic properties and the plant ecology of selected covers in the ACAP program that had both relatively high and relatively low percolation rates. The study is applying a

combination of methods to understand causes for differences in performance. The study is evaluating soil morphology, soil hydraulic properties, and occurrence of preferential flow paths; and plant community dynamics, productivity, and physiological ecology.

Future work on alternative covers will address long-term performance issues and ways to increase the sustainability of existing conventional covers. Cover environments will inevitably change in the long term in response to climate, pedogenesis, and ecological succession; changes that will not become apparent during five-year field studies. One approach for projecting long-term performance links natural analogs, modeling, and monitoring. Climate change models and natural analogs of pedogenesis and long-term ecology could be used to develop and screen possible future environmental scenarios. Parameter values for future scenarios could be input to probabilistic models that integrate performance of alternative covers and risk, such as FRAMES (Ho et al. 2004, mepas.pnl.gov/FRAMESV1). Key performance indicators would then be monitored, and the entire process would be iterated over time to refine projections as part of long-term stewardship of the site.

Finally, without intervention, pedogenesis and ecological succession will, over time, effectively transform existing conventional, low-hydraulic conductivity covers (without synthetic barriers such as geomembranes) into water balance covers. The cost of enhancing or accelerating this transformation may be less than the cost of long-term maintenance intended to prevent it. Enhancements or renovations for conventional covers could be tested in side-by-side comparisons of the renovated design and the original design using large, ACAP-type lysimeters.

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Table 1. Cover types and climate characteristics of ACAP sites: arid, semi-arid, and sub-humid locations.

Site	Cover Type (slope of test section)	Avg. Annual Precipitation (mm/yr)	Avg. Precip. /Potential Evapotrans- piration	Type of Climate [†]	Average Temp. High (mo) Low (mo) (°C)	Type of Precipitation
Altamont, CA	Monolithic barrier (5%)	358	0.31	Semi-arid	32 (Aug) 2 (Jan)	Rain, snow rare
Apple Valley, CA	Monolithic barrier (5%)	119	0.06	Arid	37 (Jul) -1 (Jan)	Rain, snow rare
Boardman, OR	Two monolithic barriers (1220 & 1840-mm thick) (25%)	225	0.23	Semi-arid	32 (Jul) -2 (Jan)	Rain & infrequent Snow
Helena, MT	Capillary barrier (5%)	289	0.44	Semi-arid	28 (Jul) -11 (Jan)	Rain & snow
Marina, CA	Capillary barrier (25%)	466	0.46	Semi-arid (coastal)	22 (Sept) 6 (Jan)	Rain
Monticello, UT	Capillary barrier (5%)	385	0.34	Semi-arid	29 (Jul) -9 (Jan)	Rain & Snow
Polson, MT	Capillary barrier (5%)	380	0.58	Sub-humid	28 (Jul) -7 (Jan)	Rain & snow
Sacramento, CA	Two monolithic barriers (1080 & 2450-mm thick) (5%)	434	0.33	Semi-arid	34 (Jul) 3 (Jan)	Rain, snow rare
Albany, GA	Monolithic barrier (5%)	1263	1.10	Humid	33 (Jul) 8 (Dec)	Rain
Cedar Rapids, IA	Monolithic barrier (5%)	915	1.03	Humid	23 (Jul) -8 (Jan)	Rain & snow
Omaha, NE	Two capillary barriers (760 & 1060-mm) (25%)	760	0.75	Humid	23 (Jul) -11 (Jan)	Rain & snow

[†]Based on UNESCO climate definitions described in UNESCO (1979).

Table 2. Soil water storage capacities and design vegetation at ACAP sites.

Site	Storage Capacities of Alternative Covers (mm)			Vegetation
	Low	Geometric Mean	High	
Omaha, NE	204	235	267	Brome and switchgrasses
	302	350	399	
Albany, GA	347	432	480	Bermuda grass, annual rye, and hybrid poplar (trees on alternative cover only)
Altamont, CA	332	373	396	Soft chess, slender oats, foxtail chess, Italian ryegrass, red-stemmed filaree, black mustard, yellow star-thistle, prickly lettuce, bull thistle, prickly sow-thistle, blue dicks, California poppy, purple owl's-clover, and miniature lupine
Apple Valley, CA	121	184	376	Creosote bush, bladder wort, Russian thistle
Cedar Rapids, IA	452	486	531	Indian grass, little bluestem, big bluestem, side oats, switch grass (conventional covers), tall fescue, hybrid poplars (alternative)
Boardman, OR				Siberian, bluebunch, and thickspike wheatgrasses, alfalfa, yellow blossom sweetclover
	493	649	745	
Helena, MT	305	392	469	Bluebunch, slender, and western wheatgrasses, sandburg bluegrass, sheep fescue, blue gramma, green needlegrass, needle-and-thread
Sacramento, CA	290	312	327	California brome, purple needlegrass, zorro fescue, arroyo lupin
	395	610	718	
Marina, CA	283	385	498	Blue wild rye, California brome, creeping wild rye, and pacific hairgrass
Polson, MT	197	250	301	Thickspike, bluebunch, slender, and crested wheatgrasses, mountain brome, Idaho fescue, Prairie junegrass, needle-and-thread, meadow brome, Canada and Kentucky bluegrasses, yarrow, fringed sagewort, alfalfa, rubber rabbitbrush, prickly rose, arrowleaf, balsamroot, dolted gayfeather, lewis flax, silky lupine, and cicer milkvetch
Monticello, UT	480	513	558	Western and crested wheatgrasses, gray rabbitbrush, sagebrush, pinyon, and juniper

Table 3. Summary of water balance data: alternative covers. Percentage of precipitation in parenthesis.

Site Location	Cover Design	Data Year (days)	Precipitation (mm)	Percolation	
				mm	As % of precipitation
Humid Sites					
Albany GA	ET	4/19/00 - 6/30/00 (73)	173*	37.7	21.79%
		7/1/00 - 6/30/01 (365)	1079*	134	12.42%
		7/1/01 - 6/30/02 (365)	1039*	3.1	0.3%
		7/1/02 - 6/30/03 (365)	1457*	218.2	14.98%
		7/1/03 - 12/31/03 (184)	594*	12.1	2.04%
		Annual Average		81	10%
* Precipitation values at Albany include irrigation of the ET cover test section.					
Cedar Rapids IA	ET	10/30/00 - 6/30/01 (269)	534	129.9	24.33%
		7/1/01 - 6/30/02 (167)	581	64.1	11.03%
		7/1/02 - 6/30/03 (365)	784	157.1	20.04%
		7/1/03 - 6/30/04 (365)	1742	365.7	20.99%
		7/1/04 - 10/4/04 (95)	181	1.14	.63%
		Annual Average		144	15%
Omaha NE	Thin ET with Capillary Break	10/5/00 - 6/30/01 (267)	448	100.1	22.34%
		7/1/01 - 6/30/02 (365)	560	3.45	0.62%
		7/1/02 - 6/30/03 (365)	475	50.9	10.72%
		7/1/03 - 6/30/04 (365)	511	68.5	13.41%
		7/1/04 - 10/3/04 (276)	293	0.31	0.11%
		Annual Average		45	9.4%
	Thick ET with Capillary Break	10/5/00 - 6/30/01 (267)	448	57.9	0.00%
		7/1/01 - 6/30/02 (365)	560	4.16	9.05%
		7/1/02 - 6/30/03 (365)	475	28.7	0.00%
		7/1/03 - 6/30/04 (365)	511	16.3	4.89%
		7/1/04 - 10/3/04 (276)	293	.66	2.85%
Annual Average		22	4.6%		

Site Location	Cover Design	Data Year (days)	Precipitation (mm)	Percolation	
				mm	As % of precipitation
Arid/Semiarid/Subhumid Sites					
Altamont CA	ET	11/10/00 -6/30/01 (231)	222	1.5	0.67%
		7/1/01 - 6/30/02 (365)	287	1.5	0.52%
		7/1/02 - 6/30/03 (365)	425	2.5	(0.59%)
		7/1/03 -6/30/04 (365)	291	64.5	(19.91%)
		7/1/04 - 10/4/04 (95)	9	0	(0.11%)
		Annual Average			14
Apple Valley CA	ET	4/25/02 -6/30/02 (66)	0	0.0	0.00%
		7/1/02 - 6/30/03 (365)	86	0.4	0.47%
		7/1/03 - 6/30/04 (365)	106	0.0	0.00%
		7/1/04 - 6/30/05 (365)	272	1.8	0.07%
		Annual Average			0.7
Boardman OR	ET Thin	12/9/00 -6/30/01 (203)	75	0.0	0.00%
		7/1/01 - 6/30/02 (365)	164	0.0	0.00%
		7/1/02 - 6/30/03 (365)	185	0.0	0.00%
		7/1/03 - 6/30/04 (365)	177	0.0	0.00%
		7/1/04 -10/4/04 (95)	20	0.0	0.00%
		Annual Average			0.0
	ET Thick	12/9/00 - 6/30/01 (203)	75	0.0	0.00%
		7/1/01 - 6/30/02 (365)	164	0.0	0.00%
		7/1/02 - 6/30/03 (365)	185	0.0	0.00%
		7/1/03 - 6/30/04 (365)	177	0.0	0.00%
		7/1/04 -10/4/04 (95)	20	0.0	0.00%
Annual Average			0.0	0.0%	

Site Location	Cover Design	Data Year (days)	Precipitation (mm)	Percolation	
				mm	As % of precipitation
Helena MT	ET with Capillary Break	10/19/1999 - 6/30/00 (225)	116	0.0	0.00%
		7/1/00 – 6/30/01 (365)	252	0.0	0.00%
		7/1/01 - 6/30/02 (365)	314	0.0	0.00%
		7/1/02 - 6/30/03 (365)	288	0.0	0.00%
		7/1/03 - 6/30/04 (365)	103	0.0	0.00%
		7/1/04 - 10/4/04 (95)	88	0.1	0.08%
		Annual Average		0.02	0.02%
Marina CA	ET with Capillary Break	7/1/00 - 6/30/01 (365)	492	44.7	9.09%
		7/1/01 - 6/30/02 (365)	401	64.2	16.01%
		7/1/02 - 6/24/03 (359)	467	51.1	10.94%
		9/27/03 -6/27/04 (274)	320	82.4	20.75%
		Annual Average		61	14%
Monticello UT	ET with Capillary Break	8/12/00 - 6/30/01 (323)	393	0.0	0.00%
		7/1/01 - 6/30/02 (365)	213	0.0	0.00%
		7/1/02 - 6/30/03 (365)	342	0.0	0.00%
		7/1/03 - 6/30/04 (365)	315	0.1	0.03%
		7/1/04 - 10/3/04 (94)	148	0.0	0.00%
		Annual Average		0.02	0.01%
Polson MT	ET with Capillary Break	11/19/99 - 6/30/00 (224)	215	0.0	0.00%
		7/1/00 – 6/30/01 (365)	358	0.18	0.05%
		7/1/01 - 6/30/02 (365)	308	0.39	0.13%
		7/1/02 - 6/30/03 (365)	326	0.19	0.06%
		7/1/03 - 6/30/04 (365)	254	0.20	0.08%
		7/1/04 – 10/4/04 (95)	87	0.0	.00%
		Annual Average		0.2	0.06%

Site Location	Cover Design	Data Year (days)	Precipitation (mm)	Percolation	
				mm	As % of precipitation
Sacramento CA	ET Thin	7/29/99 - 6/30/00 (337)	546	0.0	0.00%
		7/1/00 - 6/30/01 (365)	379	1.4	0.37%
		7/1/01 - 6/30/02 (365)	456	96.2	21.10%
		7/1/02 - 6/30/03 (365)	426	3.9	0.92%
		7/1/03 - 6/30/04 (365)	159	108.4	68.17%
		7/1/04 - 10/3/04 (94)	0.8	0.32	42.11%
		Annual Average		35	22%
	ET Thick	7/29/99 - 6/30/00 (337)	546	0.0	0.00%
		7/1/00 - 6/30/01 (365)	379	0.0	0.00%
		7/1/01 - 6/30/02 (365)	456	8.5	1.86%
		7/1/02 - 6/30/03 (365)	426	0.0	0.0%
		7/1/03 - 6/30/04 (365)	159	0.6	0.38%
		7/1/04 - 10/3/04 (94)	0.8	0.0	0.00%
		Annual Average		1.5	0.4%

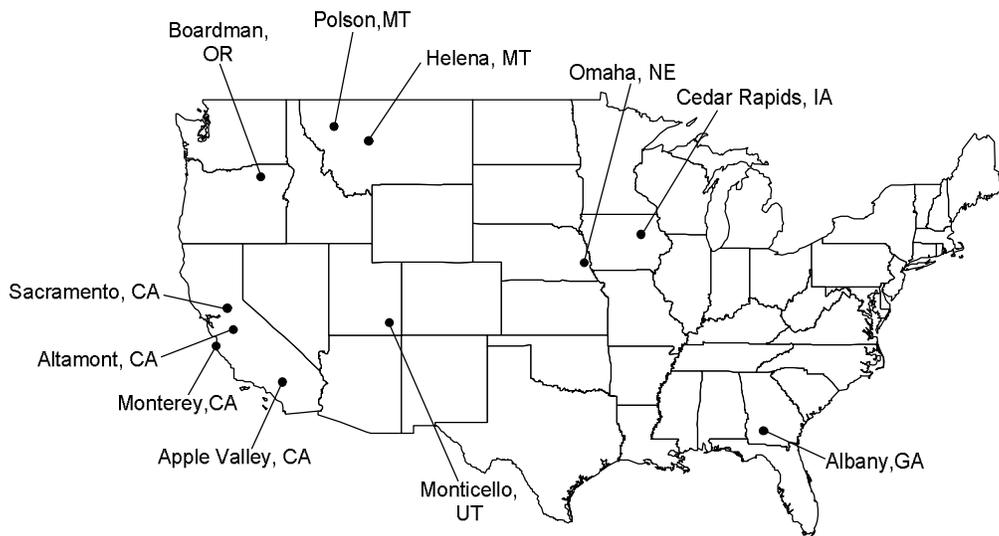


Figure 1. Locations of ACAP field sites.

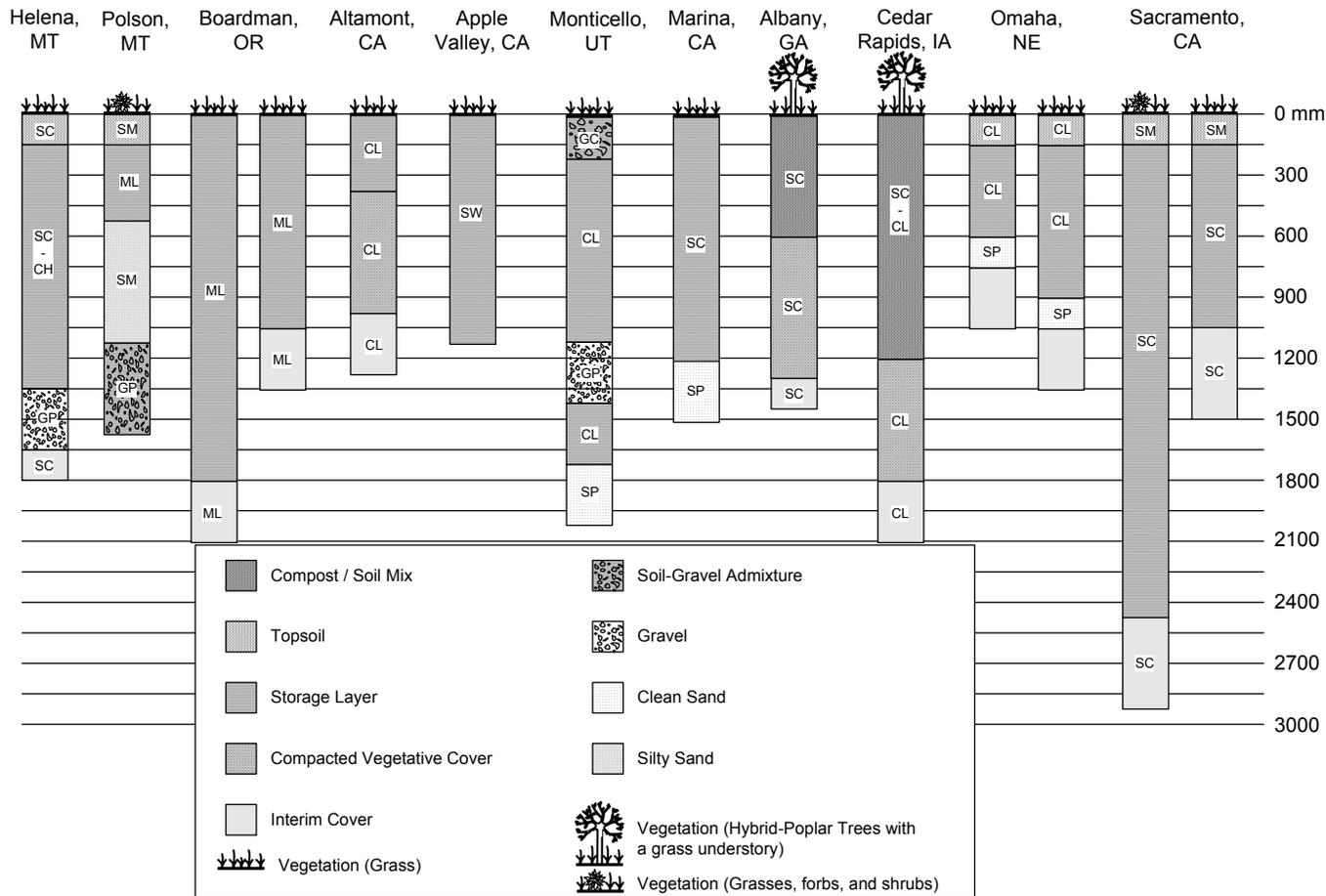


Figure 2. Profiles for alternative covers evaluated by ACAP. Two-letter designations are designations in the Unified Soil Classification System per ASTM D 2487, *Standard Classification of Soils for Engineering Purposes*: CL = low plasticity clay, CH = high plasticity clay, GC = clayey gravel, GP = poorly graded gravel, ML = low plasticity silt, SC = clayey sand, SM = silty sand, SP = poorly graded sand, and SW = well graded sand.

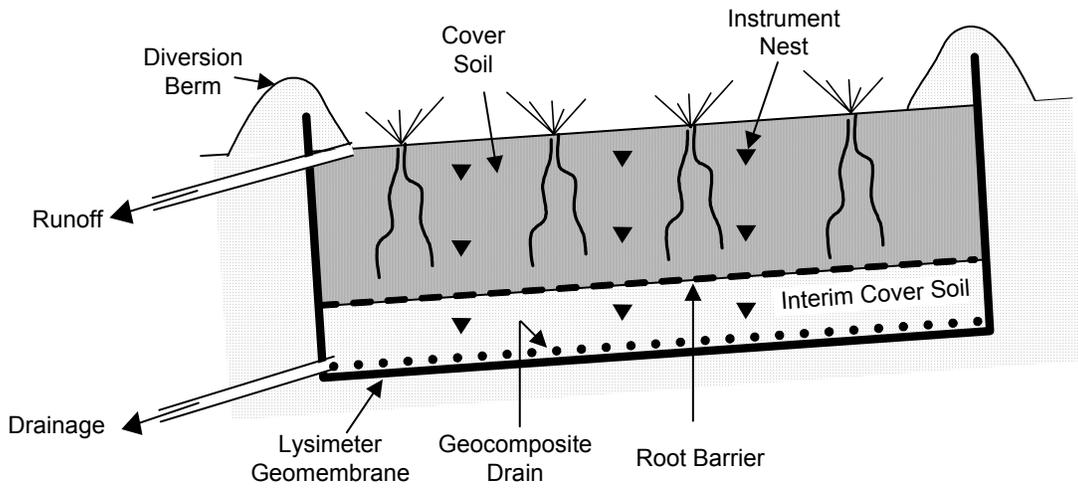


Figure 3. Schematic of lysimeter used for monitoring the water balance of the ACAP test sections.

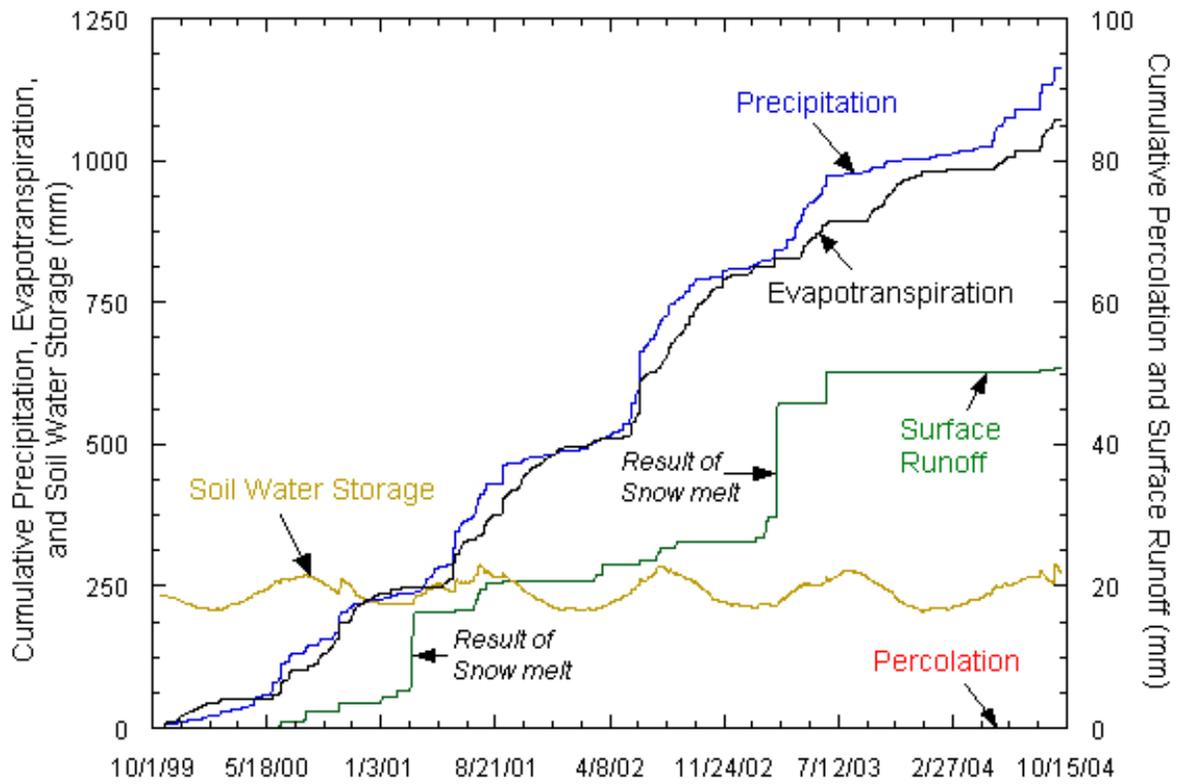


Figure 4. Water balance components of the alternative cover at Helena Mt.

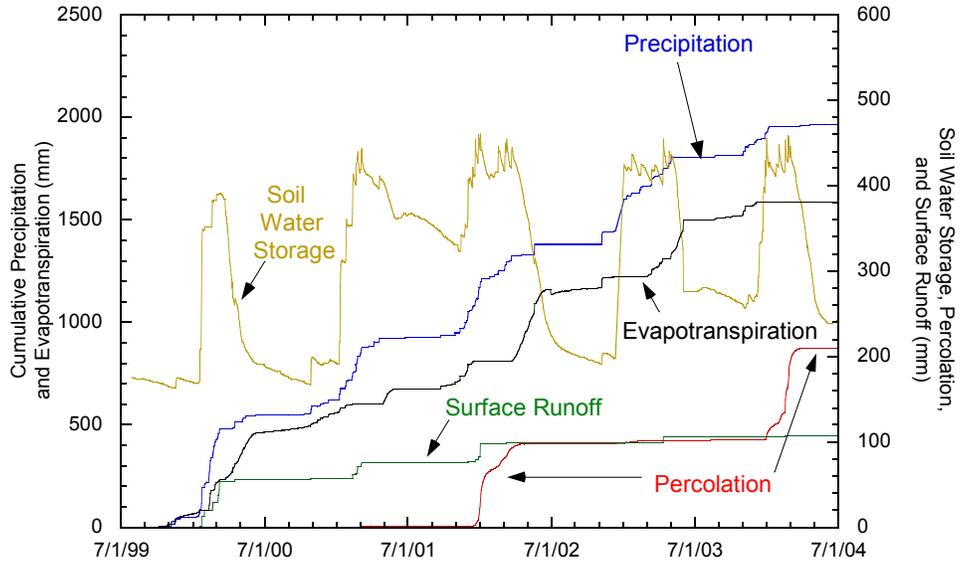


Figure 5. Water balance of the thick alternative cover at Sacramento, CA.

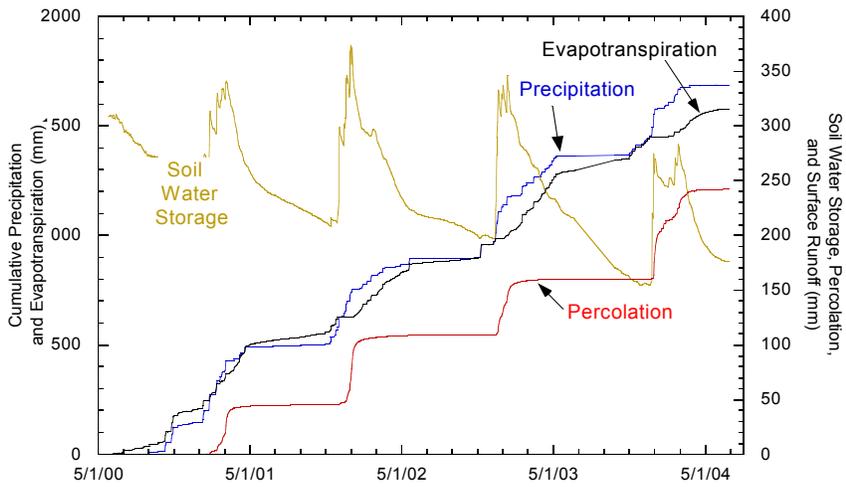


Figure 6. Water balance data for capillary barrier at Marina, CA

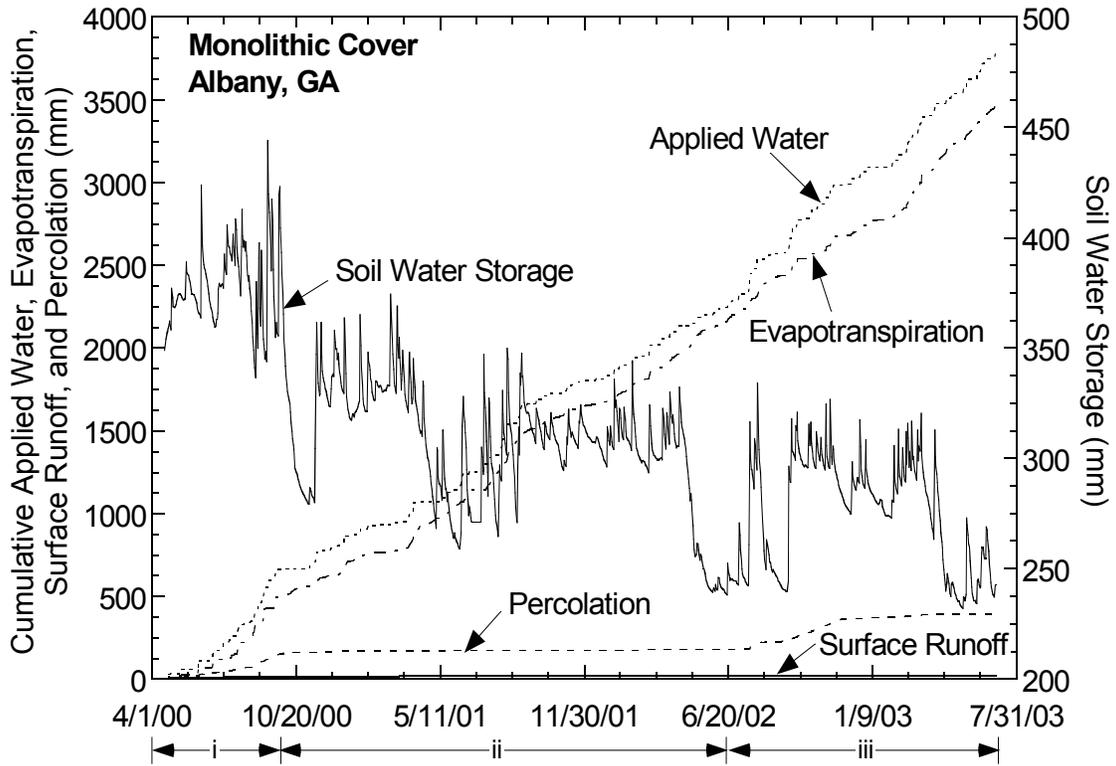


Figure 7. Water balance data for monolithic alternative cover at Albany, GA showing three distinct hydrologic periods. The three periods are indicated by the arrows at the bottom of the figure and are labeled i, ii, and iii.

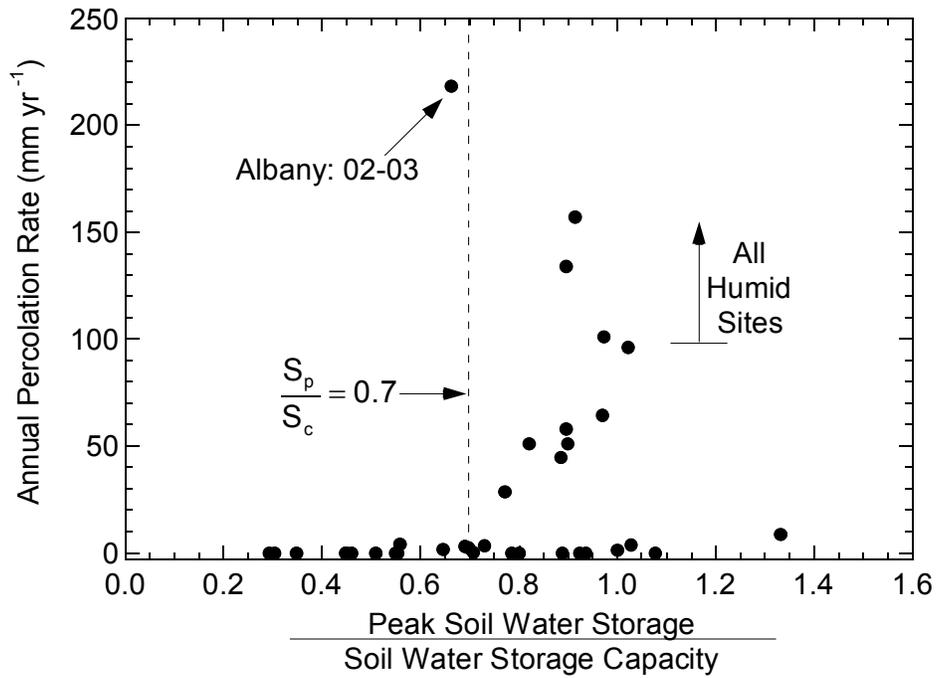


Figure 8. Annual percolation rate as a function of ratio of annual peak soil water storage to soil water storage capacity.

The impact of a RCRA-type engineered cover at an ORNL burial ground

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INTRODUCTION AND SITE HISTORY

In 1942, a rural area near Knoxville, TN became the site of major industrial facilities associated with the Manhattan Project in which processes required to produce the first atomic bombs were developed during World War II. Among other tasks, the Clinton Laboratories, the predecessor to Oak Ridge National Laboratory (ORNL - 1948), had the responsibility for developing the chemical processes for separation of plutonium from spent nuclear fuel. These activities generated a variety of hazardous and radioactive wastes, some of which was disposed in pits and trenches excavated into the subsurface. Subsequent evolution of ORNL into a multi-purpose laboratory for the Department of Energy has resulted in continued generation of both hazardous and radioactive waste that has been disposed on site. Most of the local subsurface disposal sites are located adjacent to ORNL in Melton Valley. These sites are known as Waste Area Groups (WAGs) and generally are comprised of many closely spaced, unlined pits and trenches that received the waste. One of these sites is WAG 5, which occupies a part of the watershed of Melton Branch Creek. Figure 1 is an aerial photo of WAG 5 in relation to the location of ORNL.

GEOLOGIC AND HYDROLOGIC CHARACTERISTICS OF THE SITE

ORNL is located in the valley and ridge physiographic province of east Tennessee and is characterized by thick sequences of interbedded shales and carbonate units that dip steeply to the southeast. Differences in the erodability of these units give the region its distinctive topographic features with alternating ridges and valleys. WAG 5 is underlain by at least several meters of saprolite that grades downward into weathered interbedded shale and limestone and finally into unweathered fractured bedrock. Figure 2 shows an excavated pit in the saprolite and illustrates the fact that this material retains many of the structural features of the bedrock (e.g. relicts of bedding and fractures) from which it is derived through weathering. The core material in Figure 2 is representative of the interbedded shale and limestone bedrock underlying the saprolite.

This region receives approximately 50 in/yr of precipitation of which about 10% infiltrates into the subsurface. Surface runoff represents about 40% of the precipitation with the remainder being accounted for by evapotranspiration. Groundwater flow in WAG 5 is generally to the south and discharges into Melton Branch Creek, which is located on the southern boundary of the WAG (Figure 3). There are several prominent seeps in Melton Branch where groundwater from WAG 5 discharges through fracture zones. Melton Branch joins with White Oak Creek immediately downstream from WAG 5 and their combined flow eventually discharges into the Clinch River several miles to the southwest.

NATURE AND EXTENT OF CONTAMINATION (PRE-ENHANCEMENT)

WAG 5 was the site of disposal of hazardous (e.g. cVOCs) and low level radioactive (e.g. ^3H , ^{90}Sr) waste that occurred between 1959 and 1973 in hundreds of unlined trenches and auger holes. The trenches were excavated into saprolite. Infiltrating water passes through the trenches and mobilizes soluble contaminants. In addition, seasonal variation in the depth to groundwater in WAG 5 periodically has resulted in partial flooding of some of the waste trenches, which also facilitates mobilization of

contaminants. The saprolite-bedrock environment is a dual porosity system with the fractures representing a relatively fast flow regime whereas diffusion into the low permeability matrix material creates a long-term secondary source of contaminants.

Until about 2000 there was a potential upstream source of tritium to Melton Branch Creek due to a leaking waste transfer pipe. However the leak was repaired then and essentially no subsequent losses to the creek have occurred. As a consequence, since 2000 any tritium contamination found in Melton Branch Creek adjacent to WAG 5 was released from that site. Immediately downstream from WAG 5 is an NPDES stream sampling location that has been used for many years to collect monthly compliance samples and continuous stream flow data (Figure 3). These data offer the opportunity to monitor the integrated flux of contaminants discharging with groundwater from WAG 5.

APPLICATION OF AN ENHANCEMENT

Recently, funding became available through DOE's Environmental Management Accelerated Cleanup program to hasten site cleanup activities and turn over contaminated sites to the long-term stewardship and monitoring program (U.S. Department of Energy, 1998, 1999; Bechtel Jacobs Co., 2002, 2004). As the primary vector for offsite migration of contamination in Melton Valley is surface water, the cleanup strategy at ORNL has focused on controlling discharge of contaminated groundwater to surface streams by use of extensive engineered covers.

In 2004-2005 the entire southern section of WAG 5 encompassing the trench areas was capped with a RCRA-type multi-layer cover (Figure 3). Major capping activities were completed in early fall of 2005. The area that was capped is approximately 51 acres in size that contains over 220 unlined waste trenches and nearly 100 unlined auger holes. An isolation cap was placed on the out slopes from the limits of the RCRA-type cap, as needed, to tie into the existing grade. As part of the capping activity, there was extensive grading of the area that included filling of topographic lows followed by dynamic compaction of soils. All trees (many 50+ years old) were removed from the perimeter of the waste areas, ground in a chipper, and distributed back across the waste area. Many of the trees were extremely contaminated since they have been accumulating and cycling radionuclides in their wood and leaves for decades.

The RCRA cap consists of a subgrade for the geosynthetic layers that is an uncontaminated soil material (Fig. 4). A hydraulic isolation barrier for the RCRA-type multi-layer cap overlies this contoured fill and consists of a geosynthetic clay liner, a textured 40-mil linear low-density polyethylene geomembrane liner, and a geocomposite drainage layer (clay followed by gravel). The isolation cap extends from the RCRA-type multi-layer cap to the out slope areas and consists of a 40-mil geomembrane liner, a geocomposite drainage layer, and veneer reinforcement geogrid in selected areas where slope is an issue (Fig. 4). The geosynthetic layers for both the RCRA and isolation caps were covered with 12 inches of compacted soil frost protection layer and a 6 inch vegetation layer. The cap design is such that stormflow through the drainage layer will be collected and routed to a downgradient perennial stream. The waste isolation strategy is very similar to what has been done at Savannah River Laboratory and Fernald (Chem-Nuclear Systems, 2000; U.S. Department of Energy; 2002).

IMPACT OF ENHANCEMENT ON MEASURABLE PROPERTIES

WAG 5 has been the site of extensive field research and environmental monitoring for over 10 years prior to the capping as well as during and following these remedial measures (e.g. Jardine, et al., 2000, 2006). Although this field research site lies within the footprint of the RCRA and isolation caps, the monitoring wells were allowed to remain so that information related to the impacts of cap construction and post-cap performance can be assessed. As a result, it is possible to examine several lines of evidence that address the impact of capping on the hydrology and contaminant discharges from the capped area in comparison

to baseline (i.e. pre-capping) conditions. The field site for these activities is identified in Figure 3 and included transects of monitoring wells that were completed either in fractures or matrix material. In addition to documenting the behavior of the groundwater system to precipitation events, research on the fate and transport of a variety of metals, radionuclides, and cVOCs has been carried out at this facility to document the importance of natural attenuation processes associated with redox properties of the system on the mobility of metals and radionuclides (Jardine, et al., 2002), reductive dechlorination of cVOCs (Lenczewski, et al., 2003), and matrix diffusion (Jardine, et al., 1999).

Figure 5a and b shows hydrographs for monitoring wells located in the field research site that were completed in a fracture zone and matrix material, respectively. The data are for a comparable period of time before (1999) and after (2005) capping. It is apparent that the responses of water levels to precipitation events during the two time intervals are very similar. Whereas the capping may have eliminated or greatly reduced direct infiltration, recharge on the uncapped regions of the drainage basin and even in areas in neighboring drainages probably is continuing to impact water levels under the cap. However, with regard to the hydraulic gradient under the cover, it is apparent that a significant decrease (approximately by a factor of 2) has occurred between the pre- and post-cover period (Figure 6).

Groundwater from WAG 5 discharges into Melton Branch Creek located on the south edge of the WAG. As noted above, there are no known sources of contamination entering Melton Branch upstream of WAG 5 since 2000, so that monitoring of contaminants in stream water at the NPDES sampling location near the southwest corner of WAG 5 will provide a good estimate of contaminant discharges to the stream. Stream samples are taken monthly for analysis and flow (Q) is measured continuously. Therefore, estimates of mass flux can be obtained for selected contaminants.

Tritium was among the radioactive materials placed in WAG 5 trenches and auger holes. Although tritium is considered a conservative tracer in many groundwater regimes, in the saprolite-fractured bedrock environment characteristic of WAG 5 it can diffuse into dead end pores in the rock or soil matrix (matrix diffusion) which retards its rate of migration. However, given the time elapsed since closure of WAG 5 trenches it is likely that a steady state condition exists between the mobile and matrix tritium components in groundwater. Tritium is one of the constituents that is measured at the NPDES monitoring station in Melton Branch Creek, which permits us to evaluate the mass flux of its release to the creek from WAG 5 to the receptor. Unlike the cVOC contaminants, it does not volatilize to any appreciable extent from the stream water and its measurement provides reliable information on mass flux.

Figure 7a and b illustrates monthly tritium concentrations and average monthly stream flow (Q) data from the NPDES sampling station located below WAG 5, respectively. Figure 7c presents the monthly integrated tritium flux data obtained by combining the information in Figures 7a and b. The stream flow data illustrate a clear seasonality to discharge with annual peaks that correspond to increased precipitation and runoff during late winter and spring months. By comparison the tritium concentration data do not reveal unambiguous seasonal trends. The prominent peak in tritium concentrations measured during 2004-2005 corresponds to the period of cap construction. During this time period deforestation and land grading occurred which probably led to increased infiltration and decreased evapotranspiration. In addition, dynamic compaction accompanied the grading and likely resulted in displacement of contaminated pore water resulting in its increased discharge. Collectively, these factors probably are responsible for the increased concentration of tritium in Melton Branch Creek during this time period.

The trends in tritium flux illustrated in Figure 7c reveal a strong seasonal component related to stream discharge. Note that there appears to be an increased flux of tritium associated with cap construction activities, further reinforcing the presumed causal relationship between these two factors. By late September, 2005, cap construction was largely completed. In principle, it should be possible to compare

the tritium flux subsequent to cap completion to that for an equivalent period of time in previous years to evaluate the impact of the cap on tritium releases to Melton Branch. The post-September 2005 flux record presented in Figure 7c only extends through the late April 2006 sampling period, a seven month window of time that encompasses approximately the first half of the annual flux peak observed in previous years. The integrated flux for this time window is included in Figure 7c for each cycle. Although this time interval does not intercept the annual tritium flux cycle exactly the same from year to year, it is close and represents the only means for comparison of the pre- and post-capping period of time.

The tritium data have not been corrected to a common date to compensate for radioactive decay. Of course, the total source strength for tritium in WAG 5 has declined with a half-life of 12.3 years since waste disposal ended (1973). However, the rate at which tritium becomes accessible to groundwater and transport from the trenches is unknown. There are many factors that can lead to variations in the tritium flux unrelated to decay. These include variation in the amount of precipitation (and infiltration) from year to year and the random nature of tritium release from waste containers as they deteriorate in the burial trenches. It is not possible to compensate for all of these factors, so only the raw activity data are presented in the figures.

There are two primary observations that emerge from these results. First, it appears that the integrated flux during cap construction was at least twice that of the normal flux for the same interval of time in previous years. Secondly, the integrated flux for the post-cap period (Oct. 2005 – April 2006) is only about 25 to 50% of that measured for the same time interval in previous years (excluding during cap construction). It is important to recognize that the post-cap record is very short and generalizations based on this abbreviated record must be viewed with caution. However, coupled with the observed reduction of hydraulic gradient (Fig 6), the flux reduction is consistent with a significant decline in transport of tritium from the source to the receptor stream. It will be important to follow the monthly flux measurements into the future in order to verify that the reduction is sustainable.

By mid-summer, 2006, the interceptor trench located at the southern edge of the WAG 5 cap adjacent to Melton Branch Creek was completed (Figure 3). This trench intercepts a significant fraction of shallow groundwater (and tritium) flowing under the cap before it can discharge into the creek. The collected water is pumped to a water treatment facility where it joins water from other waste areas at ORNL. The tritium concentration in stream water at the NPDES station in Melton Branch Creek dropped significantly once the interceptor trench was activated (R. Ketelle, personal communication). Consequently, it is no longer possible to use the National Pollutant Discharge Elimination System (NPDES) monitoring data to quantify the tritium flux attributable to discharge from the WAG 5 capped area after the April 2006 results illustrated in Figure 7c. It may be possible to use a combination of analytical results from the NPDES monitoring station, the interceptor trench, and/or the water treatment facility to evaluate the sustainability of the WAG 5 cap in reducing the tritium flux in the future.

INFORMATION ON THE SUSTAINABILITY OF THE ENHANCEMENT (SUSTAINED REDUCTION IN INFILTRATION, MASS FLUX, ETC.)

The key factor in evaluating the sustainability of the engineered cover at WAG 5 is its ability to limit the infiltration of precipitation into the waste trenches in the future. From the perspective of EA, as long as the cap functions well enough for long enough to control the discharging flux of contaminants within acceptable levels until such time that natural attenuation processes are fully capable of controlling the flux on their own, the enhancement is sustainable. The cap will eventually begin to fail gradually, but the most important considerations are how long before failure commences, the rate of progressive failure, and the longevity of the waste material (i.e. source strength). For example, for tritium with a 12.3 yr half-life the amount of activity in the source steadily declines over time through radioactive decay. Therefore, if the

integrity of the cap is maintained for, say, 50 yrs, the amount of activity in the source will have naturally diminished by 95%. Cap failure at that point may result in a tritium flux that stays within regulatory requirements. For the cVOC contaminants buried in the WAG 5 trenches the source strength coupled with the natural rate of reductive dechlorination will determine if the mass flux exceeds regulatory limits when the cap is in failure mode. It is important to obtain information on the cVOC degradation rates at the site as well as to monitor the integrity of the cap.

SUMMARY AND CONCLUSIONS

Construction of the engineered cover at WAG 5 appears to have reduced the integrated flux of tritium released from the WAG in the seven months immediately following emplacement of the cap. Although the apparent reduction of flux is encouraging, a much longer observation record is required to establish that the trend is sustainable. Also, the longevity of the cap before failure begins is uncertain, but is a critical factor in combination with the natural attenuation processes active in the source to determine if the release of contaminants can be maintained at levels that meet regulatory requirements.

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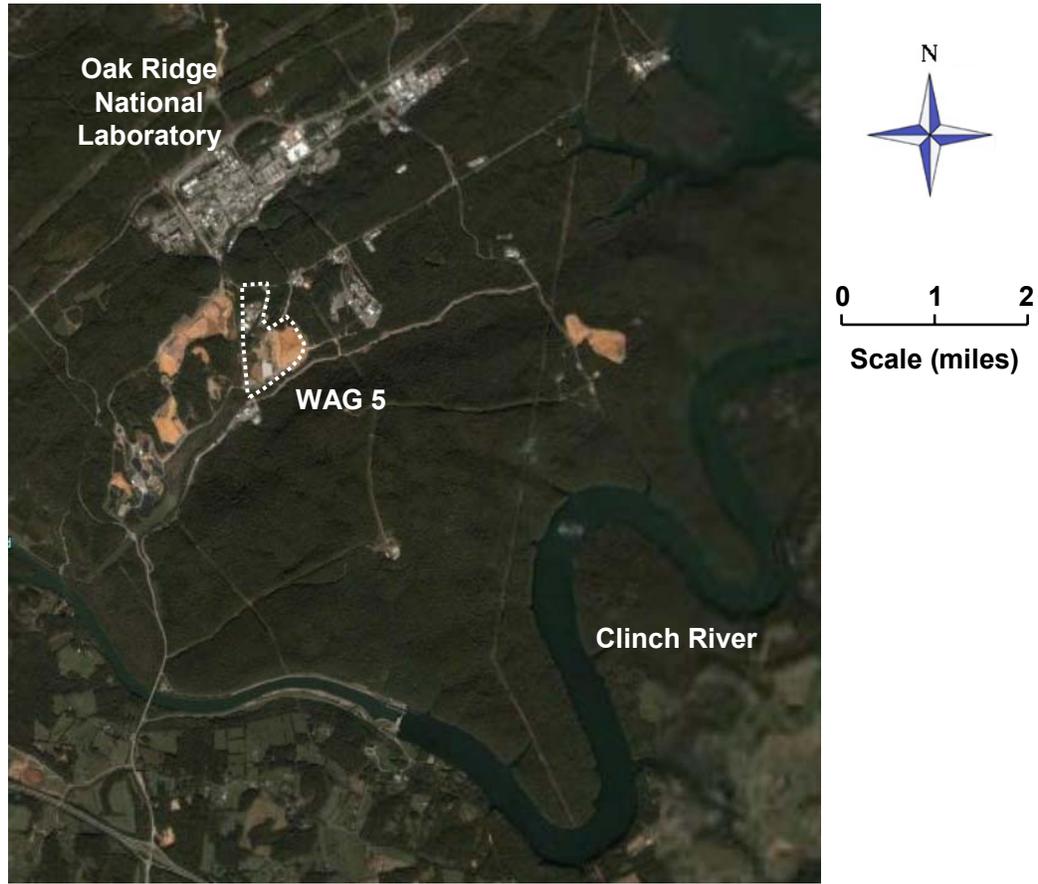


Figure 1. Location of WAG 5 near ORNL.



Figure 2. Geologic material underlying WAG 5. The photo on the left shows the saprolite in an excavated pit; the photo on the right show fractured shale and carbonate core material of the bedrock underlying the saprolite.

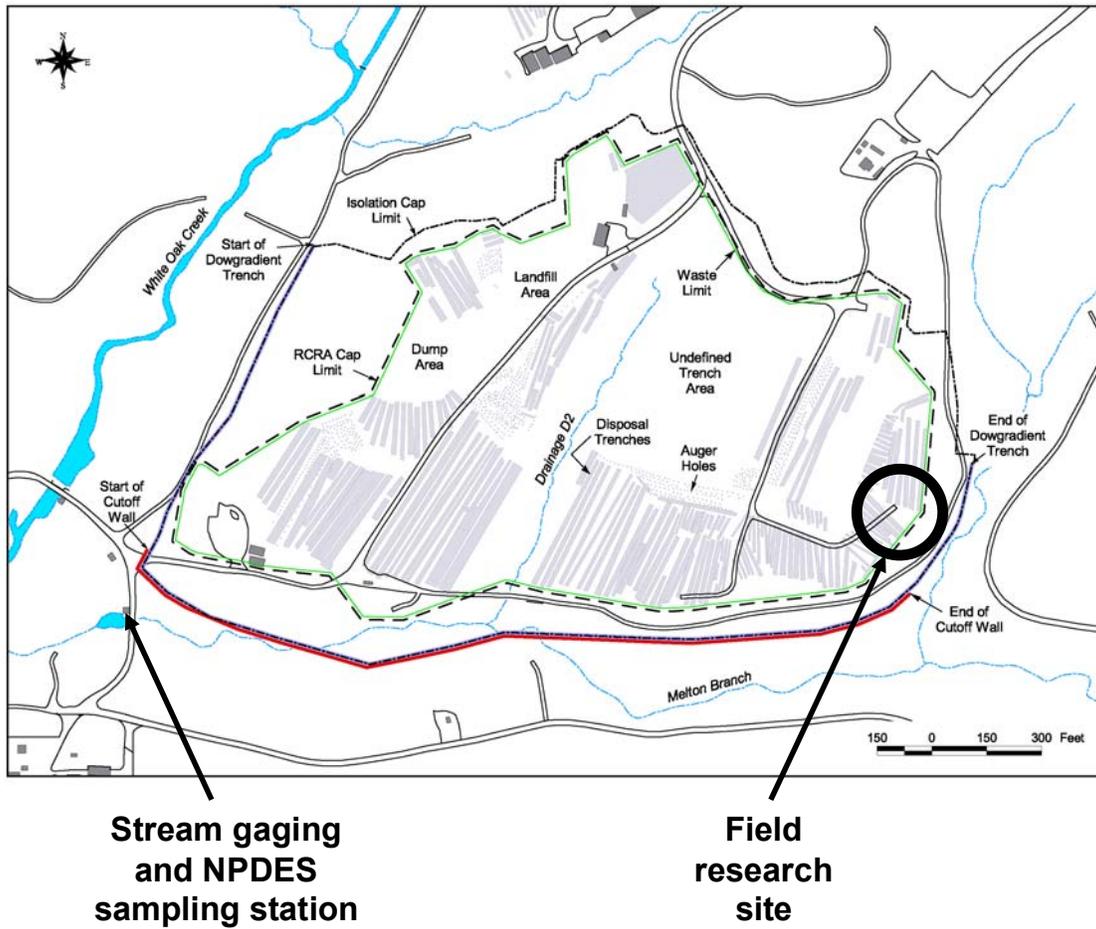


Figure 3. Details of the southern part of WAG 5 that has been capped.



Figure 4. Photograph showing the different components of the RCRA cap used at WAG 5.

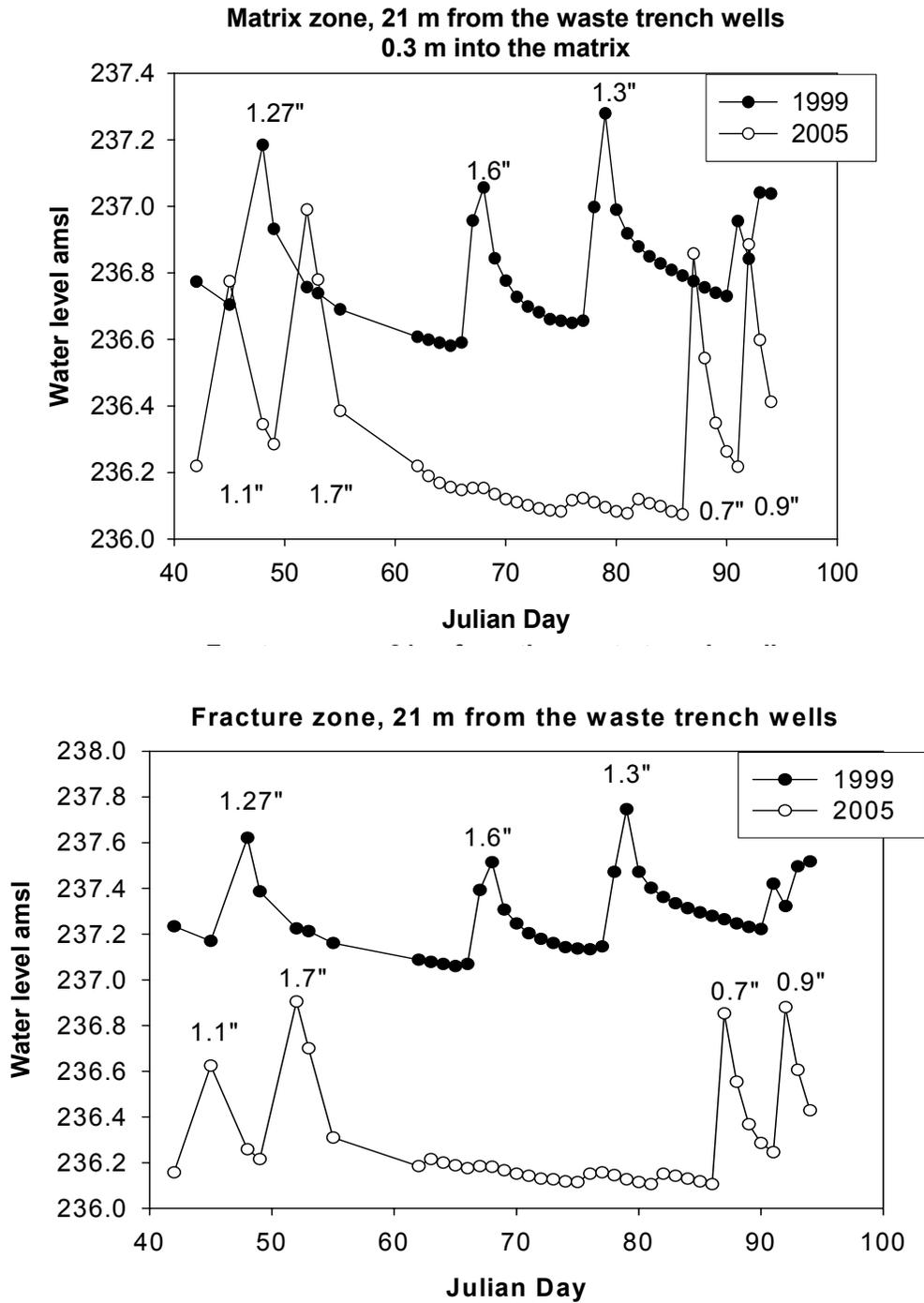


Figure 5. Hydrographs from monitoring wells located in the field research site. a) Matrix zone, b) Fracture zone. The magnitude of individual rainfall events is indicated in inches. Water level elevation is in meters above mean sea level (amsl).

Groundwater hydraulic gradient at WAG 5

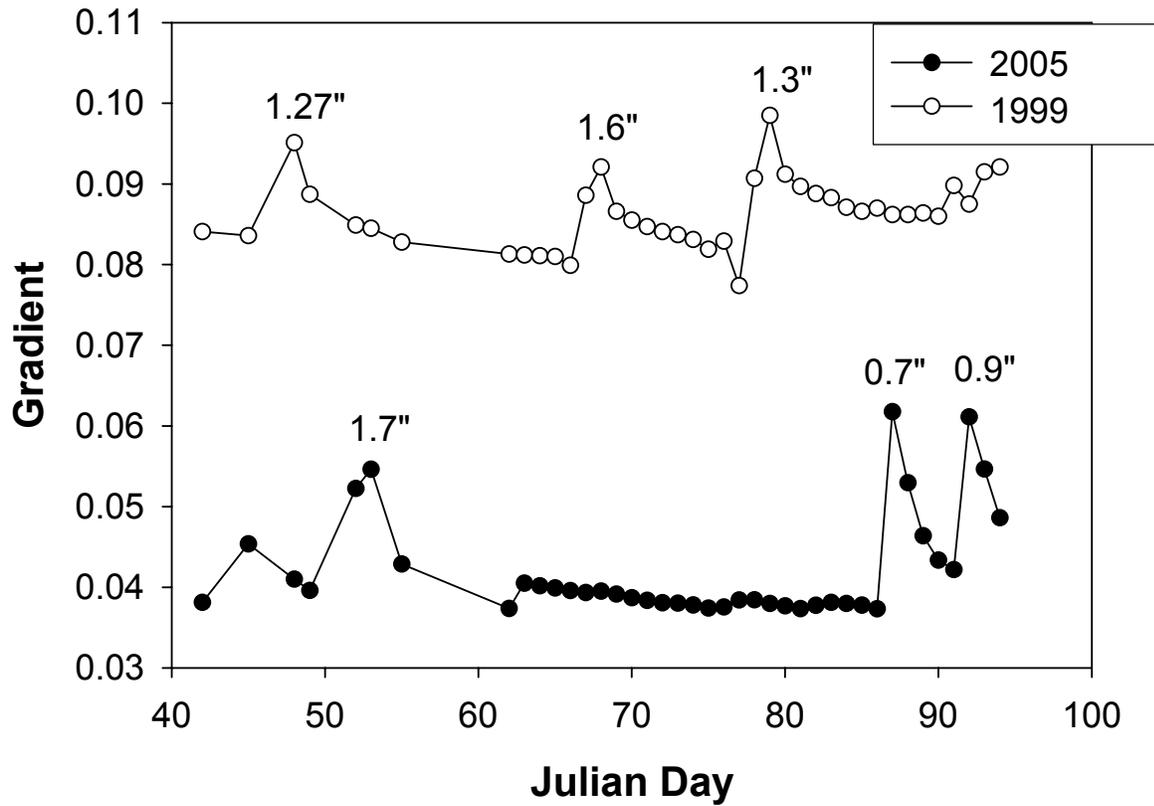


Figure 6. Comparison of the hydraulic gradient within the field research site before and after construction of the cap.

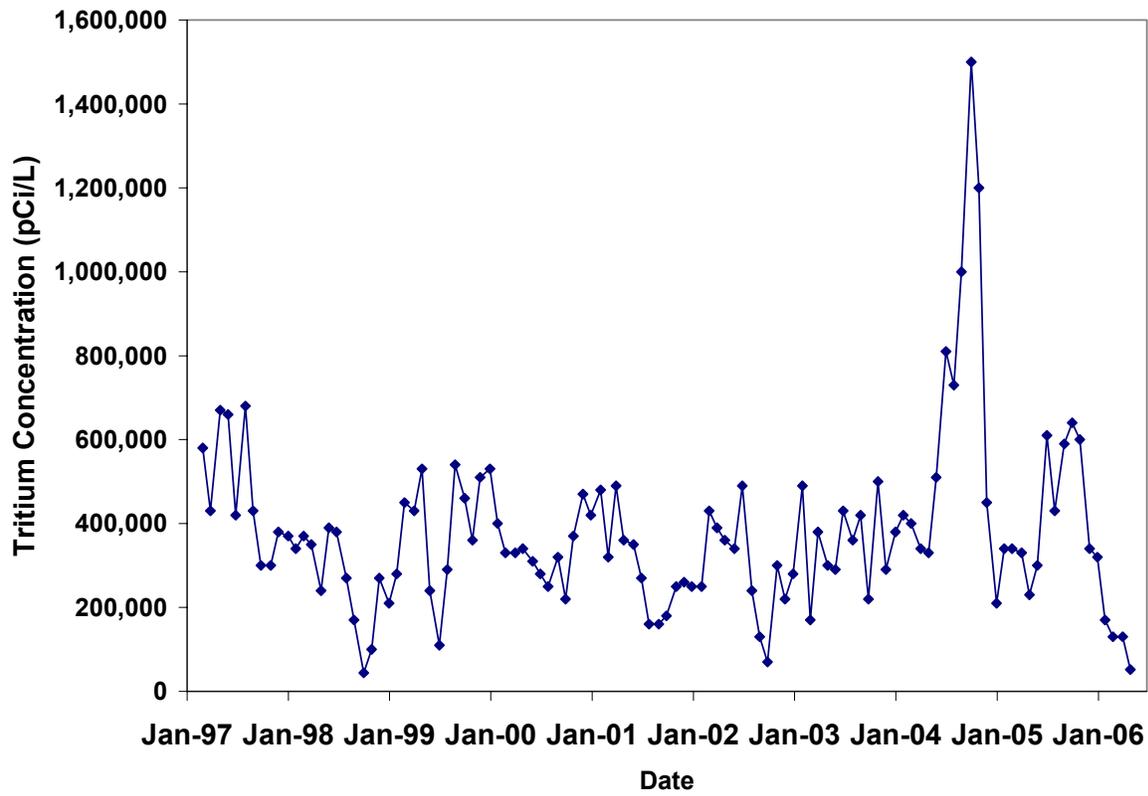


Figure 7a. Tritium concentrations at NPDES station in Melton Valley Creek immediately below WAG 5.

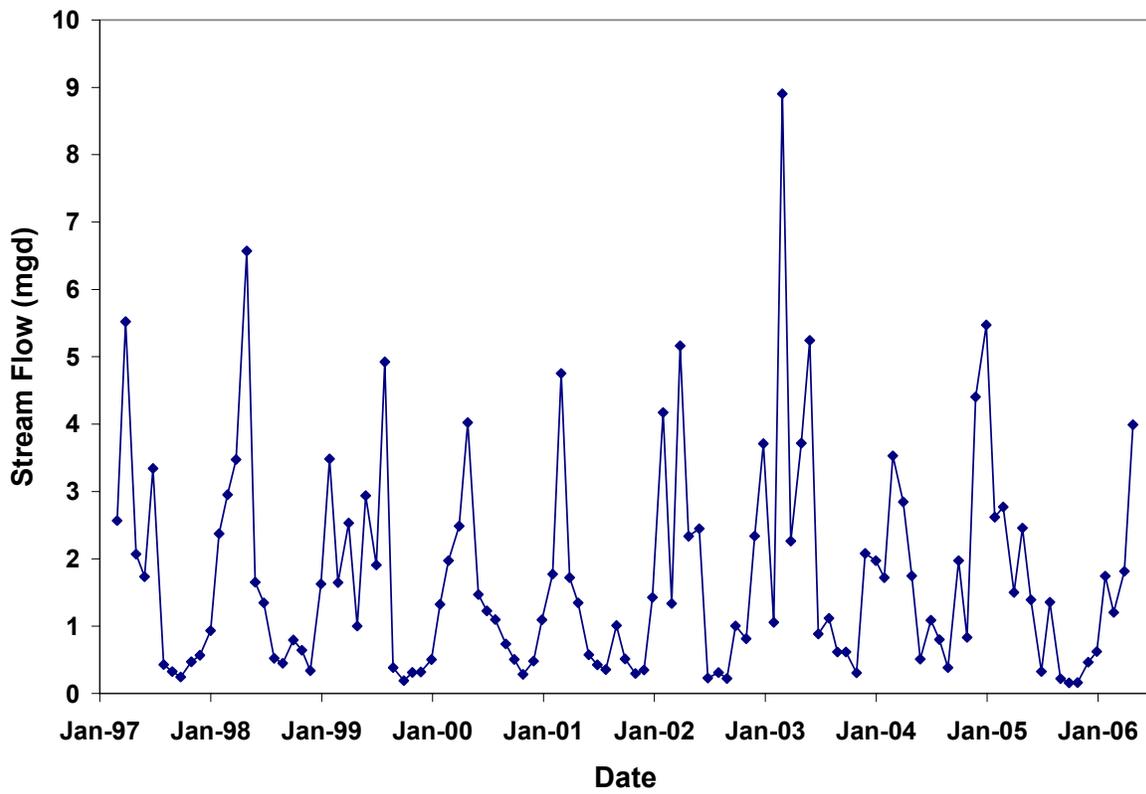


Figure 7b. Water flow in Melton Valley Creek at NPDES station immediately below WAG 5.

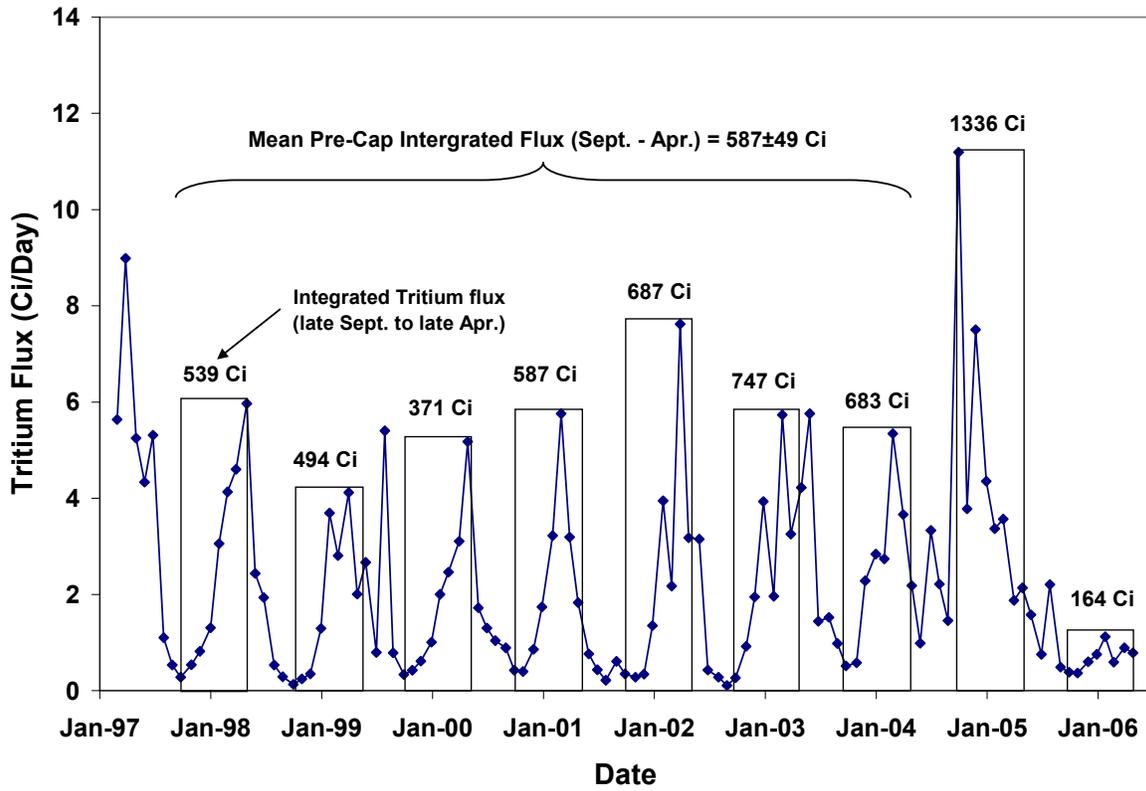


Figure 7c. Tritium flux values at NPDES station in Melton Valley Creek immediately below WAG 5. The integrated flux values are for a time window of late September to late April each year.

3.0 BIOSTIMULATION AND BIOAUGMENTATION AT CAPE CANAVERAL, FL

Introduction:

Development of techniques for bioremediation of cVOCs has been an area of active investigation for 10-15 years. Until relatively recently it was assumed that bacteria capable of biodegrading cVOCs could not survive in an environment where the dissolved concentrations of contaminants was more than a few percent of their saturation values. In the past 10 years, however, intensive research has demonstrated that some microbial species are viable in this environment. Indeed, within the last 5 years there have been promising results from some investigations indicating that bioremediation might be possible even in DNAPL source areas where dissolved concentrations of cVOCs can approach saturation levels.

This case study documents the results of a combined biostimulation-bioaugmentation demonstration at Launch Complex 34 (LC34) at Cape Canaveral, FL. This location is the site of a large source zone of dense non-aqueous phase liquid (DNAPL), TCE, underlying and in the immediate vicinity of a building that housed laboratories and metal cleaning facilities. In this project nutrients and a strain of bacteria capable of anaerobically degrading TCE to ethene was injected into a test plot located within the source zone. One of the concerns of bioremediation with EA is the possibility that an environment capable of sustaining degradation of cVOCs over a period of years might not be possible, necessitating periodic reinjection of microbes and/or nutrients to maintain treatment effectiveness. This case study establishes the proof of principle that this concern is not a problem for this site and provides optimism that sustainable bioremediation will be possible at many other contamination sites.

Enhancing the Dechlorinating Capabilities of Indigenous Microbial Consortia through Bioaugmentation

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OVERVIEW OF REDUCTIVE DECHLORINATION IN GROUNDWATER

Aerobic processes for chlorinated solvents require the addition of cosubstrates and are often limited in the concentrations of VOCs that can be treated by the low solubility of oxygen in groundwater and possible toxicity effects of intermediate byproducts on the microorganisms. While aerobic bioremediation processes are feasible under some circumstances (e.g., hydrocarbon oxidation, cometabolic biodegradation of TCE), bioremediation strategies for chlorinated solvents in groundwater typically require anaerobic redox conditions. Anaerobic reductive dechlorination does not share these limits and is the principal biodegradation mechanism for PCE and other chlorinated ethenes. Reductive dechlorination involves the step-wise replacement of individual chlorine atoms with hydrogen atoms (Figure 1) where the chlorinated ethene acts as an electron acceptor while an electron donor is required to provide energy for this process (McCarty, 1997). The end product of these dechlorination steps is ethene, which is non-toxic. Hydrogen is an important electron donor for reductive dechlorination, and is typically produced from the fermentation of other carbon substrates, such as organic acids or alcohols (Maymo-Gatell et al., 1997).

Recent research and field observations at several sites have demonstrated that TCE may be reductively dechlorinated to ethene by indigenous microorganisms in groundwater (e.g., DiStefano et al., 1991; Major et al., 1991, 1994; Ellis et al., 2000; Major et al., 2002;). Several indigenous bacteria have been identified, which directly use PCE, TCE, cis-DCE and VC as terminal electron acceptors (i.e., dehalorespiration), resulting in the production of ethene. A diverse group of organisms are reported to mediate the reduction of PCE and TCE to cis-DCE (e.g., *Dehalobacter*, *Dehalospirillum*, *Desulfitobacterium*, *Desulfuromonas*); however, only some members of the *Dehalococcoides* (Dhc) group are known to dechlorinate cis-DCE or VC to ethene. While these dehalorespiring bacteria have been identified at a number of sites, the relatively common occurrence of PCE or TCE dechlorination stalling at the formation of cis-1,2-dichloroethene (DCE) and vinyl chloride (VC) (Hendrickson et al., 2002), suggests that Dhc organisms capable of metabolic reduction of cis-DCE and ethene are not ubiquitous in groundwater environments.

A number of laboratory studies examining these dehalorespiring microorganisms have demonstrated that their activity is not inhibited at high chlorinated ethene concentrations (Table 1), suggesting that some dehalorespiring microorganisms can be active in close proximity to DNAPL. Given sufficient microbial activity adjacent to the DNAPL, the dechlorination reactions may be able to significantly enhance the DNAPL dissolution.

At field sites where the background geochemistry is generally conducive to reductive dechlorination, several engineering approaches are now feasible that may significantly increase the applicability and effectiveness of bioremediation. The process of biostimulation involves the introduction of a suitable electron donor to increase the activity of indigenous microorganisms and promote complete dechlorination to ethene. However, if the appropriate dehalorespiring microorganisms are not present, the

increase in activity may simply result in rapid degradation of the parent VOC and the accumulation of daughter products (typically either cis-1,2-DCE or VC). Accordingly, bioaugmenting the aquifer with a microbial consortium containing *Dhc* organisms capable of completely dechlorinating chloroethenes is a possible strategy for enhancing biodegradation processes. While only a few field demonstrations of bioaugmentation have been reported (Ellis et al., 2000; Major et al., 2002; Lendvay et al., 2003) each was successful at stimulating biodegradation of the target compound(s) to ethene.

While these demonstrations were effective in demonstrating that bioaugmentation was a useful approach for promoting reductive dechlorination in plumes with low chloroethene concentrations, two key questions about bioaugmentation remain unanswered:

- Can bioaugmentation be applied in DNAPL source areas where high concentrations of PCE are present?
- Is the change in dechlorination activity resulting from bioaugmentation sustained over the long-term?

The current study evaluated these questions through a pilot study conducted by United States Environmental Protection Agency's (USEPA) Superfund Innovative Technology Evaluation program (SITE), the National Aeronautics and Space Administration (NASA), and GeoSyntec Consultants at Launch Complex 34 (LC34), an unused facility at the Kennedy Space Centre.

SITE BACKGROUND

LC34 was used as a launch site for Saturn rockets from 1960 to 1968. Historical records suggest that rocket engines were cleaned on the launch pad with chlorinated organic solvents, including TCE. Other rocket parts were cleaned on racks along the west side of and inside the Engineering Support Building (ESB). During cleaning operations the solvents evaporated, infiltrated directly into the subsurface, or migrated as runoff into drainage pits. LC34 was abandoned as a launch facility in 1968 and since that time much of the site has become overgrown with vegetation.

The site location is shown in Figure 2. The Atlantic Ocean is located immediately to the east of LC34. To determine the effects of tidal influences on the groundwater system, water levels were monitored in 12 piezometers over a 50-hour period during Resource Conservation and Recovery Act (RCRA) Facility Investigation (RFI) activities (G&E Engineering, Inc., 1996). All the piezometers used in the study were screened in the surficial aquifer. No detectable effects from the tidal cycles were identified in the subject area. However, the Atlantic Ocean and the Banana River are hydraulic sinks, and groundwater likely flows toward these surface water bodies and discharges into them. Other hydrologic influences at LC34 include features such as paving, constructed drainage ditches, and topographical relief. These features may impact contaminant migration, although the impact is anticipated to be minor at the depths at which this demonstration takes place. Permeable soils exist from the ground surface to the water table and surface water tends to rapidly infiltrate to the water table.

The major water-bearing units at LC34 consist of a shallow unconfined aquifer and a semi-confined aquifer separated by a thin clay unit. The unconfined aquifer extends from the water table to approximately 45 feet below ground surface (ft bgs) and is composed of an upper sand unit (USU), a middle fine-grained unit (MFGU), and a lower sand unit (LSU; Eddy-Dilek et al., 1998). The USU is composed of medium- to coarse-grained sand and crushed shells and extends from ground surface to approximately 26 ft bgs. The MFGU, which is composed of gray, fine-grained silty/clayey sand and extends from approximately 26 to 36 ft bgs, is thicker to the north of the ESB and appears to thin to the south and west of the ESB. Below the MFGU is the LSU, which consists of gray fine to medium-sized

sand and shell fragments. The LSU contains isolated fine-grained lenses of silt and/or clay and extends to approximately 42 ft bgs.

The semi-confining clay unit (LCU) below the LSU ranges in thickness from 1 to 3 ft. While the LCU appears to be continuous in the area of the ESB and is referred to as a confining unit (CRA Services, 1999; Eddy-Dilek et al, 1998), pump test data reported by CRA Services (1999) and the recent observations of TCE in groundwater and soil samples collected below the LCU (pers. comm. from J. Langenbach, HSA Scientists & Engineers, 2003) suggest that this unit is a leaky boundary between the water-bearing units.

As may be expected, the salinity of groundwater in the shallow unconfined aquifer increases with depth with concentrations of total dissolved solids as high as 1,200 mg/L in the LSU (predominantly Na, K, Mg, Ca, Al, Cl, and SO_4/S^-). Groundwater pH is near neutral (7.3-8.0) with an alkalinity of up to 360 mg/L (as CaCO_3). Recent measurements of the groundwater oxidation-reduction potential (ORP) by GeoSyntec (unpublished data) suggest that redox conditions in the surficial aquifer are generally reducing (i.e., <-100 mV).

Limited data is available to characterize the microbial population at LC34. Eddy-Dilek et al. (1998) analyzed a limited number of soil and groundwater samples collected from the vicinity of ESB (in and outside of the DNAPL source zone) using heterotrophic plate and acridine orange direct enumeration techniques. While the limited number of samples precluded a definitive comparison, Eddy-Dilek et al. (1998) reported that the plate and acridine orange direct counts of samples collected from outside the source zone were consistent with a normal range; however, the single source zone sample was below the reliably enumerated range, suggesting that the presence of DNAPL may have inhibited microbial growth. Some evidence is available that suggests that *Dehalococcoides*-like microorganisms are present in groundwater at LC34. In May 2001 and October 2002, GeoSyntec submitted groundwater samples for analysis using molecular genetic techniques to detect the presence of these dechlorinating microorganisms and determined that *Dhc* microorganisms were present in both background and plume samples, as well as samples from the bioaugmentation pilot inside the ESB. Remediation technology demonstrations at LC34 have included performance evaluations of ISCO using potassium permanganate, six phase heating (SPH), and steam.

Nature and Extent of Contamination

The presence of DNAPL below the ESB was reported by Eddy-Dilek et al. (1998) and Battelle (1999). DNAPL source characterization efforts suggest that approximately 20,600 kg (Battelle, 1999) to 40,000 kg (Eddy-Dilek et al., 1998) of TCE DNAPL was present in the shallow unconfined aquifer near the ESB prior to the initiation of the various remediation demonstration programs at LC34. The mass of TCE DNAPL beneath the semi-confining unit is presently being investigated. Based upon groundwater concentration data collected as part of the ongoing RCRA response actions at LC34, it is evident that TCE has limited mobility in groundwater at the site (CRA Services, 1999); however, the formation of an extensive plume of cis-DCE indicates that TCE is biodegraded via anaerobic reductive dechlorination to this daughter product. Generally low concentrations (<10 micrograms per liter; $\mu\text{g/L}$) of VC are observed in groundwater.

A preliminary site investigation was conducted by GeoSyntec in June 2001 to facilitate selection of locations for the demonstration. Eight boreholes were drilled to characterize the geology, and soil and groundwater chemistry beneath the ESB. Soil samples from each borehole were field-screened using a portable photoionization detector (PID). Soil samples from three boreholes were submitted for laboratory analysis of VOCs. The results of field PID measurement and laboratory VOC analysis confirmed the

presence of DNAPL in the test plot (based on PID readings exceeding 3,000 ppmv and concentrations of TCE in soil exceeding 250 mg/kg).

STUDY APPROACH

The study evaluated the impact of biostimulation and bioaugmentation on dechlorinating activity in a test plot containing both high TCE concentrations in groundwater and DNAPL (i.e., a source zone as defined by NRC, 2004). Modification of the dechlorinating capabilities of the indigenous microbial community was completed using a two-step process. First, the redox potential of groundwater in the test plot was driven to the highly anaerobic conditions favoring the growth and activity of dechlorinating microorganisms through the addition of a highly biodegradable substrate. Second, the test plot was amended with an enriched microbial consortium containing dechlorinating organisms capable of rapid and efficient biodegradation of TCE, cis-DCE, and VC, resulting in the accumulation of ethene.

System Construction

Well installation was completed using a direct push drill rig (Precision Drilling Services). Boreholes were advanced to the target depth using a 3.5-inch diameter casing with a disposable tip. All injection, and extraction wells were constructed with 10 ft screens completed at the bottom of the USU (26 ft bgs); monitoring wells were completed with 5 ft screens. The injection and extraction wells were constructed from 2-inch inside diameter 316 stainless steel casing. Native material was permitted to collapse around the well screen and casing as the drive casing was removed. Wells were developed by purging 30 gallons (15 casing volumes) of water from each well. Each well was equipped with a dedicated Waterra® pump consisting of a Delrin® foot-valve attached to stiff, 5/8-inch outside diameter (OD) high density polyethylene tubing. Multilevel monitoring wells were installed using the same direct-push rig technique. Each multilevel was constructed of 1.5 inch OD continuous multichannel tubing with five 6-inch screened sample ports spaced at 2 ft intervals.

The treatment system includes injection and extraction wells, the above-ground treatment system, process instrumentation, and process controls. The locations of monitoring and recirculation wells are presented in Figure 3.

A tracer test was performed during startup of the system. During the tracer test, reinjected groundwater was amended for five days with bromide (KBr, Brainerd LLC of North Carolina, NC; 50 mg/L). Programmable wastewater autosamplers were employed to collect groundwater samples from MW-6 and FL-2 (two samples per day) for the purposes of generating breakthrough curves at these locations.

Culture development

The test plot was bioaugmented with KB-1™ Dechlorinator (KB-1™), a commercially-available mixed anaerobic bioaugmentation culture (SiREM, Guelph, ON). KB-1™ is comprised of four dominant microorganisms, two of which are members of the Dehalococcoides (Dehalococcoides KB-1/VC and Dehalococcoides KB-1/PCE) and present at a minimum cell density of 108 cells/L. The culture was grown using aseptic production techniques in anaerobic fermentation vessels containing a mineral medium which was amended with TCE and methanol at initial concentrations of 0.2 mM and 0.8 mM, respectively. During the production process dechlorination rates, Dehalococcoides concentrations, stability of the microbial composition, and the absence of pathogens were routinely monitored. KB-1™ was delivered to the site in two 25 L stainless steel pressure vessels (Alloy Products Inc., Waukesha, WI).

Electron Donor Amendment and Bioaugmentation

Electron donor dosing was based on providing a four-fold excess of the electron donor concentration over the minimum concentration required to reduce all electron acceptors in the recirculated groundwater (primarily TCE and sulfate). Starting on Day 76, weekly electron donor amendment consisted of a five minute pulse of 10% denatured ethanol (SDA-3, Ashland Chemical, OH) into each injection well corresponding to a time-weighted average ethanol concentration of 520 mg/L. Electron donor addition was performed throughout both the biostimulation and bioaugmentation phases.

The site was bioaugmented on 7 February 2003 with 40 L of KB-1 (108 days after the start of electron donor addition). To minimize oxygen exposure, the culture was dispensed by pressurizing the vessel with argon, pushing the culture through a submerged delivery line into the injection well. Each injection well was bioaugmented with equal volumes of KB-1 (40 L total).

Performance Monitoring

The monitoring program included bi-weekly collection of groundwater samples from the combined flow of the extraction wells, and the centerline monitoring wells for both VOC and DHG analysis. Periodic samples were also collected from the combined flow of the extraction wells and centerline monitoring wells for analysis of VOCs, DHGs, anions, and dissolved iron and manganese. Additionally, select samples from extraction wells and centerline monitoring wells were submitted for analysis of volatile fatty acid (VFA) and phospholipid fatty acids (PLFA). Groundwater samples were also collected from the multilevel wells during each phase of the pilot test, with the exact timing of these sample events based upon the results from the weekly and monthly monitoring of extraction and monitoring wells.

The primary component of the performance monitoring approach consisted of biweekly monitoring of chlorinated ethene and ethene concentrations in the centerline monitoring wells and the total extracted groundwater flow to assess trends in chloroethene biodegradation and the rate of chloroethene and ethene mass removal from the primary treatment area (PTA). During each of the three operational phases, up to three complete rounds of groundwater samples were collected from the multilevel transect sampling points for analysis of chloroethene and ethene concentrations, which were used to estimate VOC mass discharge/mass flux at the transect.

The periodic samples collected for analysis of PLFA, VFA and inorganic analytes supported characterization of changes in biomass concentration, the distribution of electron donors within the PTA, and the characterization of geochemical impacts on groundwater quality.

Analytical Methods

Chloroethene, dissolved hydrocarbon gases (methane, ethane, and ethene), *Dehalococcoides*-specific PCR assays and anion analyses were performed by SiREM (Guelph, Ontario). VFA concentrations were determined by Microseeps Laboratory (Pittsburgh, PA). Phospholipid fatty acid analysis was performed by Microbial Insights (Rockford, TN).

RESULTS

Pilot Test Hydraulic

Analysis of tracer breakthrough curves generated from monitoring wells MW-6 and FL-2 indicate that the average linear groundwater velocity along the centerline of the test plot was 0.75 ft/day (274 ft/year), corresponding to a average residence time of 24 days. Visual MODFLOW was used to simulate steady-state groundwater flow. Particle trajectories are presented in Figure 3. The model parameters included a hydraulic conductivity of 3.6×10^{-5} m/s (determined by hydraulic testing), a porosity of 0.33 and a regional gradient of 0.0001 ft/ft. Particle trajectories confirmed that flow in the test plot was principally horizontal at a recirculation rate of 1.5 gpm. Based on the modelling analysis, residence times in the test plot ranged from 25 days through the centerline (which corresponds to that estimated by the tracer test) to 32 days along the edges.

Groundwater Geochemistry

A summary of background geochemistry in the test plot is provided in the Table 2. Following electron donor addition, groundwater redox potential generally decreased to about -200 mV. Measurable concentrations of ethanol were not observed in any groundwater samples, indicating that this substrate was rapidly fermented by indigenous microorganisms to acetate, propionate, butyrate and hydrogen. Following electron donor amendment biomass concentrations in groundwater samples increased approximately 10-fold to 10^5 - 10^6 cells/mL (based on PLFA analysis). Minimal utilization of acetate occurred within the test plot and acetate breakthrough occurred at the extraction wells 108 days following the start of electron donor addition. Although dissolved iron and manganese are present in the background groundwater, the concentration of these constituents did not increase within the test plot, suggesting that there was not a significant mineral-phase reservoir of these reductants.

The average baseline sulfate concentration in the test plot was 315 mg/L. Following electron donor addition, the concentration of sulfate decreased concurrently with TCE dechlorination, with a maximum sulfate concentration of 11 mg/L, indicating an increase in the activity of sulfate-reducing microorganisms. Sulfate concentrations in the reinjected groundwater were consistently greater than 70 mg/L; however, during the period of electron donor addition, sulfate reduction was sufficiently rapid that sulfate was only detected in only the two monitoring wells closest to the injection wells (MW-3 and PA-26).

The activity of methanogens was of particular interest, especially given the potential problems of inefficient electron donor usage and aquifer fouling resulting from the formation of methanogenic biomass and methane exsolution (Yang and McCarty, 2002). The average methane concentration observed during the baseline monitoring period was 0.5 mg/L. During most of the period of electron donor addition methane concentrations did not increase; however, an increase in methanogenesis occurred once the chloroethene concentrations had decreased sufficiently (maximum methane concentration 21 mg/L, MW-6). The apparent inhibition of methanogenesis in the presence of excess electron donor is consistent with the results of our microcosm data and prior studies indicating that methanogenesis is readily inhibited at comparable chloroethene concentrations (e.g., DiStefano et al., 1991; Lee et al., 1997; Kennes et al., 1998; Yang and McCarty, 2002).

TCE Dechlorination and Inhibition

The results of chloroethene and ethene monitoring at the centerline monitoring wells are summarized in Figure 4. In general, similar time trends were observed in each of the monitoring wells. During the baseline phase TCE was the dominant chloroethene (average concentration of 253 mg/L) with much lower concentrations of cis-DCE (3 mg/L). Following the addition of electron donor and bioaugmentation, TCE concentrations rapidly decreased while ethene concentrations increased substantially throughout the test plot. At the end of the demonstration, the average ethene concentration in the test plot was 66 mg/L (2.4 mM), which is approximately an order of magnitude greater than the ethene concentration previously reported to inhibit methanogenesis (Yang and McCarty, 2002).

The extent of reductive dechlorination was quantified by calculating a dechlorinating score for each sample collected from test plot monitoring wells. For each sample the dechlorination score was calculating as the average molar fraction of chlorine removed from the initial concentration of the parent compound (i.e., TCE), based on the concentration of TCE and less-chlorinated ethenes (including ethene) in each sample, using:

$$\text{Dechlorination Score } N_D = \left(1 - \frac{3[TCE] + 2[cisDCE] + [VC]}{3([TCE] + [cisDCE] + [VC] + [Ethene])} \right)$$

where the parentheses indicate molarity, and a dechlorination scores of 33, 66, and 100% represent complete conversion to either cis-DCE, VC or ethene, respectively. A summary of dechlorination scores throughout the study is provided in Figure 5.

Under intrinsic conditions, only limited dechlorination of TCE to cis-DCE occurred ($N_D < 0.04$). During the period of active Enhanced *in situ* Bioremediation (EISB) treatment, the extent of dechlorination (as shown in Hood et al., 2006) increased rapidly. During the initial period of electron donor amendment, dechlorination resulted in the accumulation of cis-DCE and VC. Following test plot bioaugmentation, the extent of dechlorination shifted past cis-DCE and VC, with ethene comprising the dominant biodegradation product. Following the period of active EISB treatment, the system was decommissioned with only ambient groundwater flow through the test plot. Groundwater samples collected 22 months following system shutdown indicate that the significant extent of dechlorination was sustained in the absence of continued electron donor addition. There were no detections of TCE (Figure 4), confirming that VOC concentrations did not rebound after the period of active groundwater treatment and ethene remained the dominant degradation product in the test plot. However, there was an ~20-fold decrease in the total chloroethene concentration, suggesting that there is a significant ethene sink. Under highly methanogenic conditions, biodegradation of ethene to CO₂ via anaerobic oxidation can occur (Bradley and Chappelle, 1999; Dolfing, 1999) and this is a potential reactive sink for ethene in LC34 groundwater. These data suggest that bioaugmentation resulted in a sustained shift in the microbial community towards organisms capable of efficient cis-DCE and VC dechlorination.

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Parent Compound	Concentration		Reference
	mg/L	mM	
Tetrachloroethene	232	1.4	Adamson et al. (2004)
Tetrachloroethene	199	1.2	Nielsen and Keasling (1999)
Tetrachloroethene	149	0.9	Yang and McCarty (2000)
Tetrachloroethene	133	0.8	Duhamel et al. (2002)
Tetrachloroethene	100	0.6	Isalou et al. (1998)
Tetrachloroethene	91	0.5	DiStefano et al. (1991)
Tetrachloroethene	58	0.3	Lee et al. (1997)
Tetrachloroethene	27	0.2	Kennes et al. (1998)
Trichloroethene	1,105	8.4	Nielsen and Keasling (1999)
Trichloroethene	267	2.0	Hood et al. (2006)
Trichloroethene	297	2.3	Yang and McCarty (2000)
Trichloroethene	197	1.5	Duhamel et al. (2002)
Trichloroethene	170	1.3	Harkness et al. (1999)

Table 1. Maximum chloroethene concentration resulting in reductive dechlorination in microcosm studies. Note that the reported aqueous solubility's of tetrachloroethene and trichloroethene are 232 mg/L and 1,100 mg/L, respectively (Pankow and Cherry, 1996).

<i>Parameter</i>	<i>Baseline</i>	<i>Final</i>
Chloride (mg/L)	182	185
Nitrate-N (mg/L)	<0.6	<0.6
Bromide (mg/L)	<2.3	<2.3
Sulfate (mg/L)	315	5
Orthophosphate (mg/L)	<3.8	<3.8
Acetate (mg/L)	<1.0	178
Butyrate (mg/L)	<1.0	6
Propionate (mg/L)	<1.0	40
pH	7.3	6.9
Specific Conductivity ($\mu\text{S}/\text{cm}$)	1,292	2,645
Temperature ($^{\circ}\text{C}$)	30	28
Dissolved Oxygen (mg/L)	<0.1	<0.1
Oxidation-reduction Potential (mV)	-128	-171

Table 2. Summary of pre- and post-demonstration groundwater geochemistry.

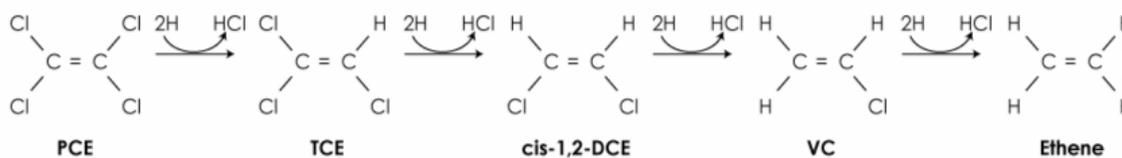


Figure 1. Pathway for reductive dechlorination of PCE and TCE to ethene.

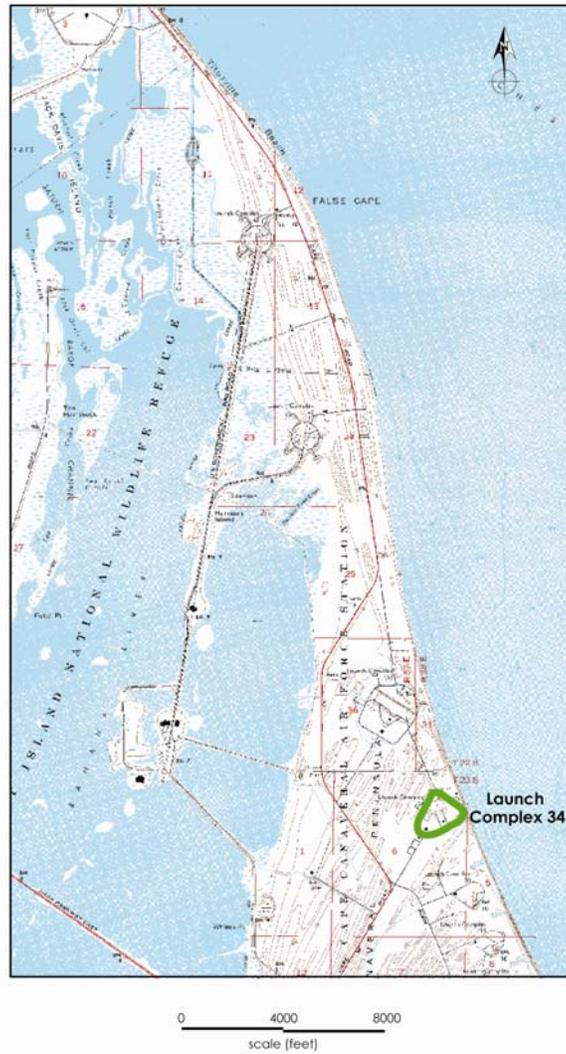


Figure 2. Location of Launch Complex 34 at the Kennedy Space Center, Florida.

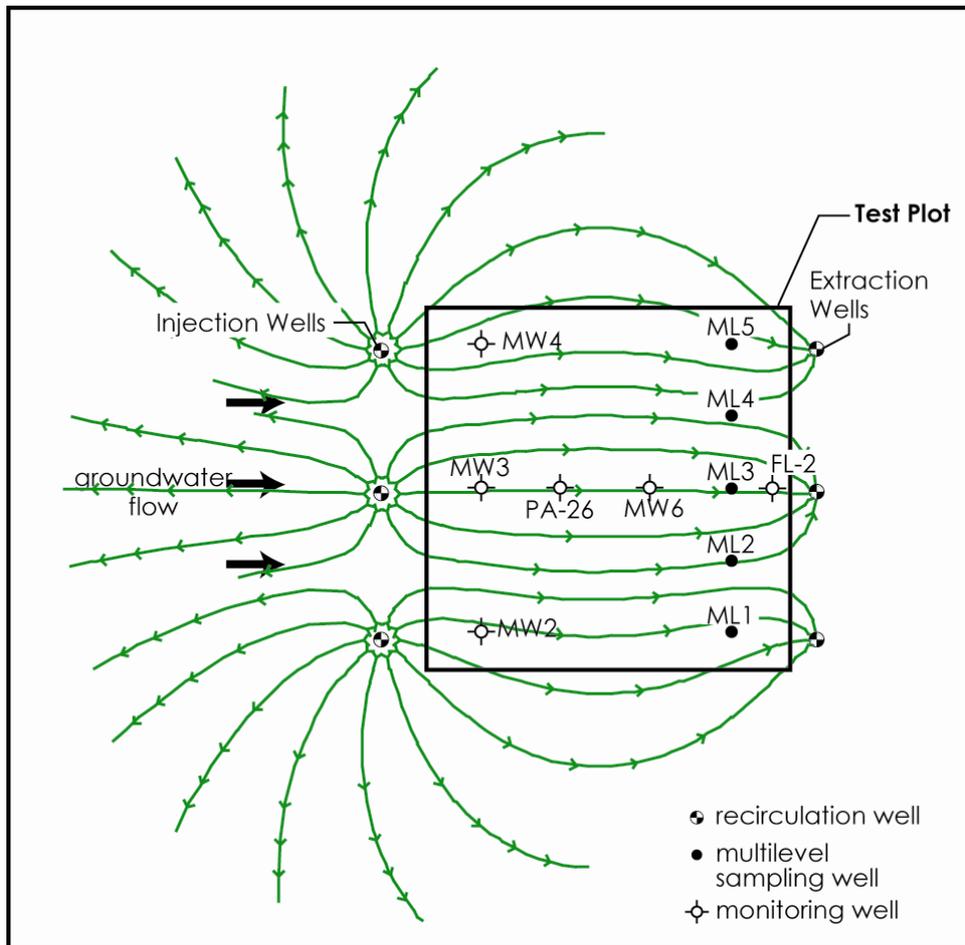


Figure 3. Site layout, showing the locations of injection and extraction wells, monitoring wells and multilevel monitoring wells (arrows on particle trajectories indicate five days travel time).

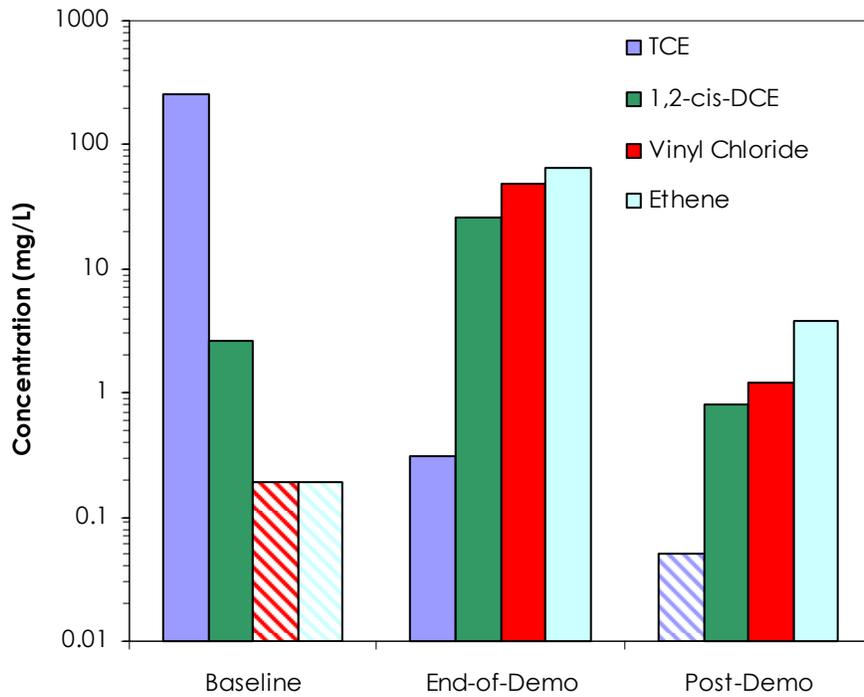


Figure 4. Average concentrations of TCE, cis-DCE, VC and ethene in the centerline monitoring wells (MW-3, PA-26, MW-6, and FL-2) in the test plot during the Baseline, End-of-Demonstration and Post-Demonstration (22 months after shutdown) phases of the study. Diagonal hatchmarks represent non-detect concentrations of the given constituent.

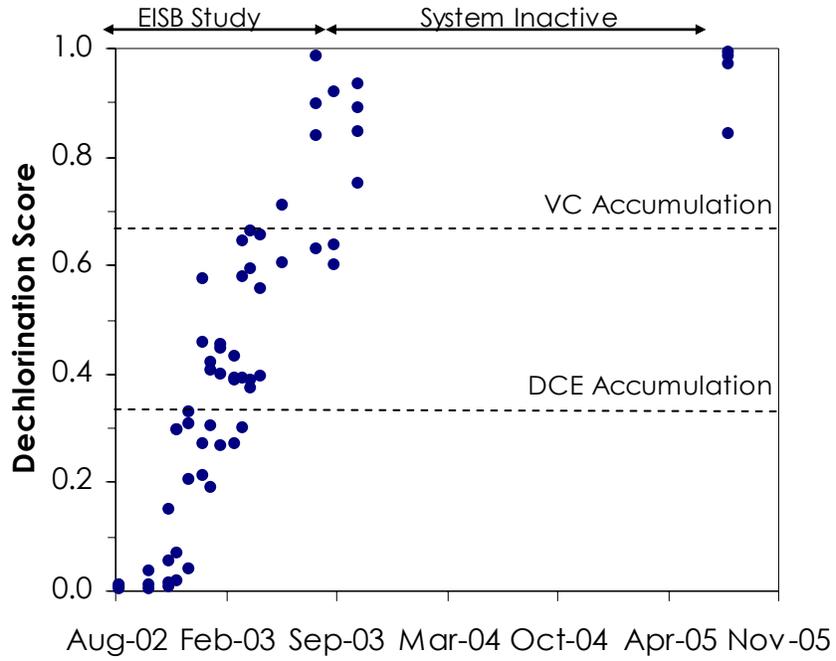


Figure 5. The extent of dechlorination in all monitoring wells. Box-and-whiskers represent the minimum, first quartile, median, third quartile, and maximum values (n=23; dashed lines at 33 and 66% represent complete conversion of the parent TCE to either -DCE or VC, respectively).

4.0 PERMEABLE REACTIVE BARRIERS

Introduction:

In 1991 the University of Waterloo installed the first pilot-scale, trench-type permeable reactive barrier at Canadian Forces Base Borden in Ontario Canada (Gillham and O'Hannesin, 1992). The reactive medium used was zero valent iron (ZVI) and for 15 years this PRB has proven to be an effective, passive technology for treating a groundwater plume contaminated with TCE. Numerous other pilot- and full-scale permeable reactive barriers (PRBs) have been deployed and have yielded important information about the design, selection of reactive media, reaction mechanisms, and potential operational problems.

Most PRBs use ZVI as the reactive media, although a variety of other metals and metal alloys have been investigated. By the late 1990s organic-based materials were being tested as reactive media for chlorinated volatile organic contaminants (cVOCs), including wood chips, mulch, etc. In general, zero-valent metals function as electron sources to cause abiotic reductive dechlorination of cVOCs, although it was recognized early that the generation of hydrogen through reaction of Fe and water could promote growth of anaerobic bacteria that could facilitate microbial degradation of cVOCs in these types of PRBs. Mulch and other similar organic media also act as sources of electrons and primarily serve as substrates to stimulate growth of anaerobic bacteria that biodegrade the contaminants.

Permeable reactive barriers often have been promoted as a potential method of achieving regulatory-driven clean-up criteria for groundwater contaminated with cVOCs and some PRBs appear to be successful in meeting this objective. However, with enhanced attenuation the goal is to view PRBs and other potential enhancements as a passive, sustainable method of reducing contaminant concentrations (or, more properly, contaminant mass flux) in a plume to a level that yields a stable or shrinking plume. Consequently, the enhancement augments natural attenuation processes already at work in the aquifer system to achieve a favorable outcome that will meet regulatory approval.

This section is comprised of two case studies that are examples of full-scale permeable reactive barriers used to treat cVOCs in groundwater. The first example is for a traditional ZVI-type of barrier that was installed at the US Coast Guard Station at Elizabeth City, NC in 1996 by researchers at EPA's Ada, OK laboratory and other collaborating scientists and has been monitored carefully since then. This PRB has been used to treat cVOCs and Cr(VI).

The second case study involves a full-scale treatment wall using a mulch-sand mixture that was deployed by the Air Force Center for Environmental Excellence (AFCEE) at Offutt AFB in July 2001 to treat groundwater contaminated with TCE. The period of intensive post-emplacement performance monitoring occurred between 2001 and 2003. The period of monitoring for both PRBs, while somewhat limited relative to the projected life of the walls, does provide preliminary information that addresses the issue of sustainability.

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Zero-Valent Iron Permeable Reactive Barrier, U.S. Coast Guard Support Center, Elizabeth City, NC¹

O.R. West (Geo Consultants, LLC, Knoxville TN)

1. SITE DESCRIPTION AND HISTORY

The U.S. Coast Guard Support Center (USCG-SC) is an active Coast Guard base located approximately 5 km southeast of Elizabeth City, North Carolina on the southern bank of the Pasquotank River (**Fig. 1**). A former electroplating shop approximately 60 m from the Pasquotank River (**Fig. 2**) was in operation for 30 years until it was closed in 1984. Subsequent environmental investigations revealed the presence of chromium (Cr) contaminated soils underlying the plating shop, as well as a shallow (<8 m depth) groundwater Cr plume that extends from the plating shop towards the river (**Fig. 2**). Trichloroethylene (TCE, **Fig. 3**), cis-1,2-dichloroethylene (cis-DCE) and vinyl chloride (VC) were later found to be also present in the groundwater. The chlorinated solvents are likely from historical degreasing operations conducted at the USCG-SC.

A zero-valent iron (ZVI) permeable reactive barrier (PRB) was installed at the site in June 1996 to intercept the Cr plume as well as to treat part of the laterally more extensive chlorinated solvent plume (see **Figs. 2** and **3**). At the time the barrier was installed, ZVI-PRB technology was a relatively new concept which had been proven in laboratory-scale experiments to create a highly reducing environment that resulted in Cr immobilization and dehalogenation of TCE and other chlorinated solvents. Extensive monitoring of the Elizabeth City PRB from 1997 through 2001 was conducted by the U.S. Environmental Protection Agency (EPA) as part of the agency's research efforts to better understand ZVI-PRB long-term performance. Groundwater wells and multilevel samplers were installed in and around the vicinity of the PRB and were used to periodically collect groundwater samples. The groundwater samples were analyzed for contaminants and other water chemistry parameters to evaluate the impact of the PRB on the groundwater system and its effectiveness for removing target contaminants. In addition, cores from the PRB were collected periodically from 1997 through 2001 for chemical, mineralogical and microbiological analysis to characterize and assess the extent of corrosion, mineral precipitation and biomass build-up that affect long-term PRB performance. The results of these sampling efforts have been documented in several reports including Blowes et al., 1999a, b and c; Wilkin et al., 2003; Paul et al., 2003. This case study contains a summary of information and data from these reports and other related publications (Sabatini et al., 1997, Wilkin et al., 2002, Wilkin et al., 2005).

2. GEOLOGIC AND HYDROLOGIC SETTING

The Elizabeth City PRB site is underlain by typical Atlantic coastal plain sediments comprised of heterogeneously distributed sands, silts, and clays. In general, the upper 2 m of the aquifer consist of sandy to silty clay, while the deeper sediments are silty to clayey fine sands with interbedded silty clay lenses. The surficial aquifer is bounded at 18 m (~60 ft) depth by the dense clays of the Yorktown Confining Unit (Blowes et al., 1999a).

¹ R. Wilkin, U.S. Environmental Protection Agency, Office of Research and Development, was consulted during the preparation of this case study.

Groundwater levels in monitoring wells screened 3 to 4.5 m below groundwater surface (bgs) ranged from 1.5 to 2.1 m bgs, according to annual measurements from 1991 through 1994 (before PRB installation; Blowes et al., 1999a). These water level measurements indicate that shallow groundwater generally flowed northward towards the Pasquotank River, with average hydraulic gradients varying between 0.0011 and 0.0033 (Blowes et al., 1999a). Hydraulic conductivity measurements from slug testing in wells screened 4.5 to 7.6 m bgs ranged from 0.09 to 4.84 m/day with a median of 1.5 m/day (before PRB installation; Sabatini et al., 1997). Groundwater velocities obtained from tracer tests, also conducted before the PRB was installed, were 0.13 and 0.15 m/day (Puls et al., 1995 as referenced in Blowes et al., 1999a).

Sabatini et al. (1997) report that the observed Cr plume is not moving as fast as predicted using measured hydraulic conductivities and gradients. It was suggested that tidal effects from the Pasquotank River could have resulted in hydraulic gradient reversals and slower plume movement. However, Sabatini et al. (1997) also notes that continuous water level monitoring over a three month period indicated only small and infrequent disturbances in the regional gradient.

3. NATURE AND EXTENT OF CONTAMINATION (PRE-ENHANCEMENT)

The Cr groundwater plume emanating from the former electroplating shop (**Fig. 2**) is a result of leaking acidic chromium solution that was discovered in 1988. Cr-contaminated sediments underneath the electroplating facility have since been removed, however subsequent environmental sampling showed groundwater chromium concentrations in excess of the maximum contaminant level (MCL) of 0.05 mg/L (Blowes et al., 1999a). Using a network of 40 monitoring wells, the extent of the Cr plume where concentrations exceeded the MCL was found to be 7 m deep, 35 m wide, and 65 m long extending from Hangar 79 towards the Pasquotank River (see **Fig. 2** which shows the Cr plume upgradient of the PRB). TCE groundwater contamination, which was first discovered in 1991, is laterally more extensive than the Cr plume (compare **Figs. 2 and 3**). TCE was commonly used as a degreasing solvent prior to electroplating. However, the specific source for TCE contamination at the Elizabeth City PRB site is not well defined, unlike the Cr plume which was clearly linked to a leaking Cr solution from the former electroplating shop. Groundwater grab sampling using cone penetrometers conducted in 1994 indicated TCE contamination at depths below 7.3 m (below the maximum depth of the PRB). Blowes et al. (1999a) reported that the areal and vertical extent of the TCE plume had yet to be determined, and acknowledged that the PRB only addresses a portion of this TCE plume (see **Fig. 3**).

4. APPLICATION OF THE ENHANCEMENT

The Elizabeth City PRB was installed in June 1996 using a continuous trenching machine which was capable of simultaneously excavating sediments while emplacing granular iron into the excavation. During the PRB design phase, laboratory experiments were conducted on a number of granular iron sources to determine reaction rate coefficients for TCE degradation and chromium removal (see Blowes et al., 1999a for discussion of laboratory testing results). Based on lower cost and adequate reaction rates, granular iron from Peerless Metal Powders, Inc. (grain sizes ranged from 0.25 to 1 mm, average grain size of 0.4 mm) was chosen over the other granular iron sources tested.

The design depth of the PRB was 7.3 m, which corresponds to the maximum excavation depth of the trenching machine used at the site. The top of the ZVI material in the PRB was set at ~2.0 m bgs so that the ZVI remains below the water table. The Elizabeth City PRB is a "hanging wall" because it is not "keyed" into a low permeability zone, which exists approximately 10 m below the bottom of the PRB (dense clays of the Yorktown confining unit).

Based on the design dimensions of the PRB (ZVI from ~2 to 7.3 m depth, 0.6 m thick, 46 m wide) and the bulk density of laboratory-packed ZVI test columns, a total of 450 tons should have been emplaced. However, the trenching machine was only able to pour 280 tons of granular iron into the excavation. The discrepancy may be due to a difference in bulk density between the laboratory-packed ZVI test columns and field-installed ZVI, as well as slumping of the excavation walls during barrier installation (Blowes et al., 1999a). In situ electrical conductivity was used to assess the continuity of the emplaced ZVI in the PRB. This approach is based on the large difference in electrical conductivity between natural aquifer material and granular iron. The resulting distribution of electrical conductivity on a plane parallel to the long axis of the PRB indicated a spatially variable distribution of ZVI within the PRB. At the eastern end of the PRB, the emplaced ZVI appears to be continuous from ~2 m bgs to 7.3 m bgs (as designed), whereas ZVI near the middle and on the western end of the PRB is less continuous.

Slug testing in and near the PRB ~ 6 months after the barrier was installed showed a wide range of hydraulic conductivities (**Fig. 4** for transect 2; see **Fig. 2** for transect location) which was attributed to the installation technique (Blowes et al., 1999b). As a result of the lower mass of iron emplaced in the PRB, some hydraulic conductivities were much higher than that measured in laboratory-packed columns (85 m/day). Low hydraulic conductivities near the upgradient aquifer/PRB interface (0.01 to 0.08 m/day, **Fig. 4**) were attributed to mixing of aquifer material with granular iron and slumping of the trench walls during iron emplacement (Blowes et al., 1999b).

5. IMPACT OF ENHANCEMENT ON MEASURABLE GROUNDWATER PROPERTIES

Periodic groundwater and solid material/core sampling from 1997 through 2001 after PRB installation provided extensive information regarding the long-term impact of the PRB on the groundwater system. Groundwater samples were collected from a sampling network that includes (1) monitoring wells upgradient and downgradient of the PRB ("MW" in **Fig. 2**) with screen lengths ranging from 1.5 to 2 m, and depths ranging from 4.5 to 19.2 bgs, and (2) multilevel samplers ("ML" in **Fig. 2**) that consist of bundled sampling tubes designed to sample from ~3 to ~7 m depth at ~0.5 m intervals. The multilevel samplers are arranged along "transects" that run perpendicular to the long axis of the PRB and parallel to anticipated groundwater flow.

Fig. 5 shows TCE concentrations from monitoring wells (marked by "MW" in **Fig. 2**) located upgradient (**Fig. 5a**), ~2 m downgradient (**Fig. 5b**), and within 10 m of the Pasquotank River (**Fig. 5c**). TCE concentrations as high as 1625 µg/L were measured in MW-48 located approximately 2 m upgradient of the PRB and screened from ~4 to 7.3 m bgs. In downgradient wells MW-47 and MW-49 which are screened at the same depths as MW-48, TCE was above 5 µg/L (MCL) but generally remained below 10 µg/L throughout the 5 year monitoring period following PRB construction. On the other hand, TCE concentrations in MW-50 have exceeded 100 µg/L during most of the sampling events. MW-50 is screened from ~8 to 9.7 m bgs, and may be reflecting deeper TCE contamination flowing under the PRB. TCE concentrations in MW-46 (screened from 4 to 7.3 bgs) and MW-52 (screened from 3.4 to 9.5 m bgs) were greater than 100 µg/L and may also be reflecting contamination flowing under or around the PRB. As mentioned previously, it was acknowledged at the onset that the PRB was designed to capture the Cr plume and only a portion of the laterally more extensive and less well defined TCE plume. Cr, with upgradient concentrations in monitoring wells as high as 4.7 mg/L in MW-13 was effectively removed by the PRB to levels below MCL (0.05 mg/L) in downgradient monitoring wells, as reported by Blowes et al., 1999b and Wilkin et al., 2003.

TCE degradation in groundwater that flows through the barrier can also be evaluated using data from the multilevel samplers ("ML" in **Fig. 2**). For this case study, data from transect 2 is presented (**Fig. 6**, see **Fig. 2** for transect location), where the highest TCE groundwater concentrations were measured at the

PRB site. The multilevel sampling bundles in transect 2 include ML21 (~2 m upgradient of the PRB), ML23.5 (at the upgradient "fringe" interface of the aquifer and PRB), ML24 (within the PRB), and ML25 (~1.5 m down gradient of the PRB). The distance between bundles ML21 and ML25 is ~3.4 m, and the maximum sampling depth in each bundle is ~7-7.2 m bgs (i.e., at or above the maximum depth of the PRB). TCE concentrations in ML21 were as high as 9040 µg/L, measured in 2000 at 7.0 m bgs (**Fig. 6a**). At ML23.5, ML24 and ML25, TCE concentrations drop significantly from upstream values to below 100 µg/L but appear to gradually increase with time (**Figs. 6b-d**). The latter may be due to increasing upgradient TCE concentrations over time observed in ML-21 (**Fig. 6a**), although it is not possible to rule out decreasing PRB reactivity.

In addition to TCE, the removal of other target contaminants is also summarized in **Table 1**, while other water quality parameters measured in transect 2 are presented in **Table 2**. The tables show the minimum and maximum values based on all depths and sampling events for each multilevel sampling bundle. Lower concentrations of cis-DCE are evident in the downgradient sampling bundles ML24 and ML25. The presence of ethene and ethane in ML23.5, ML24, and ML25 is evidence for dechlorination occurring as groundwater moves through the PRB. Methane concentrations, which were only measured in 1997 and 1998, showed significant increases from upgradient values of <100 µg/L in ML21 to maximum concentrations greater than 4000 µg/L in ML23.5, ML24, and ML25. Molar concentrations of methane (max. of 330 µM) exceed the combined molar concentrations of TCE, cis-1,2-DCE and vinyl chloride (<100 µM) suggesting another source for methane generation. To explain the observed methane production in the PRB, Blowes et al. (1999b) cited a hypothesis by Hardy and Gillham (1996) that methane is produced from the reduction of CO₂ by ZVI. Experiments by Deng et al. (1997) suggest that hydrocarbon production in iron/water systems (even in the absence of dissolved chlorinated organics) is primarily from the conversion of carbon present as carbide impurities in the ZVI. Another possible source for methane observed at the Elizabeth City PRB is methanogenesis by bacteria from dissolved CO₂ using elemental iron as the electron source. The latter process was demonstrated by Daniels et al. (1987) in experiments wherein CH₄ was produced in iron/water/CO₂ systems inoculated with methanogenic bacteria but was not observed in uninoculated and sterilized controls.

Of the other parameters measured, groundwater pH, Eh, sulfate and nitrate were markedly altered by the PRB (**Table 2**). The increase in pH and decrease in Eh as groundwater moves through the PRB are expected from the corrosion reaction of ZVI with dissolved oxygen and water. The removal of sulfate and nitrate is also an expected result of reducing conditions in the vicinity of the PRB. Groundwater pH increased from background values of 5.4 - 6.4 at ML21 to maximum values of 10.7 within the PRB (ML24), and remained slightly higher than background downgradient of the PRB (6.38 - 9.84 at ML25). A detailed plot of pH vs time in transect 2 (**Fig. 7**) shows that although upgradient pH remains relatively constant throughout the monitoring period (ML21, **Fig. 7a**), pH appears to be decreasing with time in the upgradient fringe area (ML23.5, **Fig. 7b**) and within the PRB (ML24, **Fig. 7c**). This trend may be an indication of reduced ZVI reactivity with time, which Wilkin et al. (2003a) also suggest based on contour plots of Eh data. Background Eh stayed consistently positive at ML21 throughout the monitoring period (1997-2001), while Eh values as low as -554 mV were measured within the PRB at ML24.

Fig. 8 contains plots of Eh vs time from transect 2, and shows significant spatial and temporal variations in Eh within the PRB (ML24, **Fig. 8c**). Downgradient of the PRB (ML25, **Fig. 8d**), spatial and temporal variability is no longer as pronounced and Eh values are generally lower than background conditions (ML21, **Fig. 8a**). From contour plots of Eh along transect 2, Wilkin et al. (2003a) observe that the zone with Eh values below -100 mV has progressively decreased from 1997 through 2001 and suggest that this indicates decreasing reductive capacity with time. This observation is consistent with **Fig. 8c** (ML24), which shows Eh values in the deeper intervals (6, 6.5, 7 m bgs) fluctuating between positive and negative values from 1997 through 1998, and staying positive from 1999 through 2001.

Alkalinity upgradient of the PRB (ML21, **Fig. 9a**) appears to be stratified with higher values observed in the shallower depths (4 to 4.5 m). Within the PRB (ML24, **Fig. 9c**), alkalinity drops significantly at the shallower depths (4 to 5.5 m) but remains comparable to background conditions at greater depths (compare **Figs. 9a** and **9c**, 6 to 7 m). The difference between upgradient (ML21) and downgradient (ML24) conditions is consistent with carbonate precipitation that is expected to occur under the high pH conditions within the PRB (Wilkin et al. 2003a). On the other hand, plots of alkalinity vs time show elevated alkalinity in the upgradient fringe zone relative to background values during the most recent sampling events (ML23.5, **Fig. 9b**). This increase in alkalinity may be related to microbial activity in the upgradient fringe zone, as shown by elevated microbial mass concentrations measured using phospholipid fatty acid analysis (PLFA) on solid cores collected from the PRB site (**Fig. 10a**).

Other parameters (specific conductivity, dissolved cations) are not presented in this case study but are discussed in Wilkin et al., 2003. In general, specific conductivity and dissolved cations decrease as groundwater flows through the barrier, consistent with mineral precipitation that is expected to occur in the high pH, low Eh environment within the PRB.

6. SUSTAINABILITY OF THE ENHANCEMENT

The primary factors that influence the long-term performance of ZVI-PRB are sustained reactivity and hydraulic efficiency. Data from the multi-level samplers that span the depth of the PRB showed continuous removal of dissolved TCE and Cr within the PRB over the 5-year monitoring period. However, based on Eh values in some locations within the PRB that appear to be increasing with time, the PRB may be gradually losing its ability to produce reducing conditions needed for reductive degradation of TCE and other chlorinated contaminants. TCE detected in monitoring wells downgradient of the PRB and screened below the maximum depth of the PRB indicates that the deeper groundwater plume is not being captured by the barrier.

Changes in hydraulic efficiency of the Elizabeth City PRB with time were evaluated through quantitative estimates of carbonate and sulfide precipitation in solid samples collected from the PRB annually from 1998 through 2000 (Wilkin et al., 2003). Inorganic carbon and sulfur were analyzed in the solid samples (**Fig. 10b** and **10c**, showing distribution in 2000), and relative precipitate volumes were calculated assuming the carbonate and sulfide precipitates consisted of aragonite, siderite and mackinawite. Porosity loss was then assumed to equal the precipitate volume less porosity gain due to iron dissolution. These calculations resulted in an estimated porosity loss rate of 0.75% per year assuming that mineral precipitation occurs within the front 8 cm of the PRB. Note however that these calculations do not include iron oxides and hydroxides that were also observed in mineralogical analyses of solid samples (Blowes et al., 1999b). Furthermore, biomass buildup at the upgradient aquifer/PRB interface indicated by PLFA analysis (**Fig. 10a**) is likely to even further decrease the hydraulic efficiency of the PRB.

Water levels in the monitoring wells measured in 1997 through 1999 indicate that water generally flows across the PRB (Wilkin et al. 2003). However, the number and coverage of the monitoring wells for which water levels were measured are probably too small to discern changes in the capture zone of the PRB brought about by mineral precipitation and biomass buildup.

7. SUMMARY AND CONCLUSIONS

Analysis of data from extensive monitoring of the Elizabeth City PRB shows the following:

- Over the 5-year post-construction monitoring period, TCE and other chlorinated compounds were effectively degraded from groundwater that flowed through the PRB. Residual concentrations were still above MCLs but were significantly below the upgradient values. Cr was also effectively removed. TCE detected downgradient of the PRB and in deeper wells (> 7.3 m) is likely from the deeper contaminant plume flowing under the PRB.
- Ethene and ethane were detected in and downgradient of the PRB, providing evidence for dehalogenation reactions occurring within the barrier. In addition, methane was measured two years after the PRB was installed and was quantified at elevated molar concentrations that suggest a source other than the influent chlorinated organic contaminants. Possible mechanisms for methane generation include CO₂ reduction by ZVI, conversion of carbide impurities in the granular iron, and bacterial methanogenesis using ZVI as an electron donor.
- Significant changes in pH and Eh relative to background conditions occurred in the upgradient fringe area, within the PRB, and persisted ~1.5 m downgradient of the PRB. Gradually increasing Eh within the PRB suggests that reactivity within the PRB may be decreasing. Increasing TCE in the PRB may be due to this gradual change in reactivity although increasing upgradient TCE concentrations cannot be ruled out. In general, there is a decrease in alkalinity as groundwater approaches and flows through the PRB. However, in more recent sampling, alkalinity was observed to increase above upgradient values in the upgradient fringe zone. This increasing trend in alkalinity may be related to microbial activity.
- Decreases in alkalinity, specific conductivity, and dissolved cations within the PRB relative to background conditions reflect mineral precipitation that was confirmed by mineralogical analysis of solid core samples. Porosity loss over time was estimated to be around 0.75% per year, based on inorganic carbon and sulfur concentrations measured in the solid samples, assuming precipitates were carbonate (i.e., aragonite, siderite) and sulfide (i.e., mackinawite) minerals. Note that this estimate does not include precipitation of iron oxides and oxyhydroxides which were also detected in the mineralogical analyses of the solid samples. Furthermore, biomass buildup was observed at the upgradient aquifer/PRB interface which likely also negatively impacts the hydraulic efficiency of the PRB.

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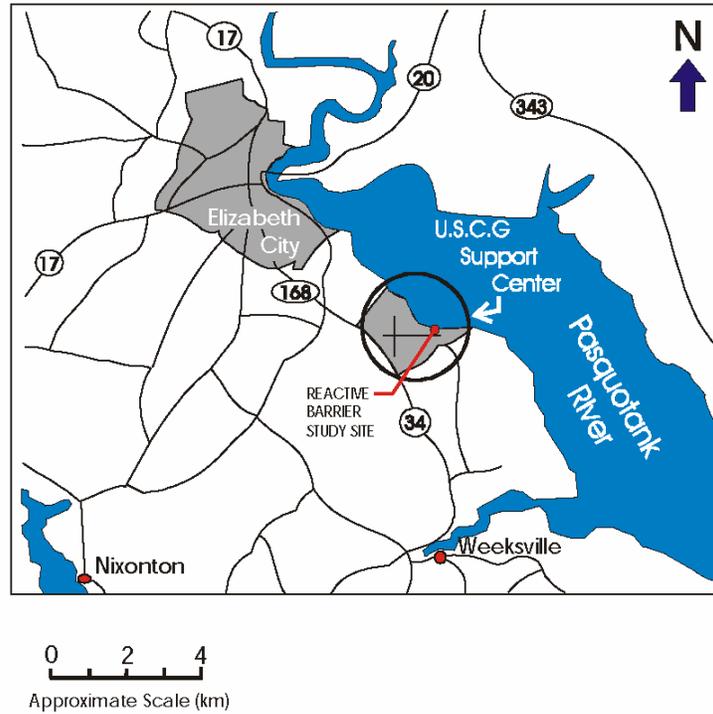


Figure 1. Location of permeable reactive barrier at U.S. Coast Guard Support Center, Elizabeth City, N.C. (from Blowes et al., 1999a).

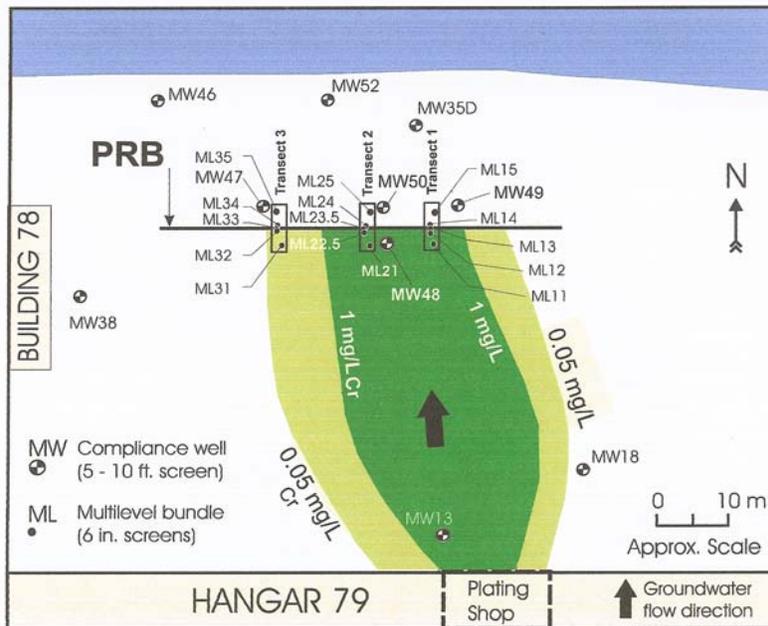


Figure 2. Site map showing the location of a former electroplating shop which is the source of a groundwater chromium (Cr) plume. Map also shows permeable reactive barrier (PRB) and network of monitoring wells (from Wilkin et al., 2003).

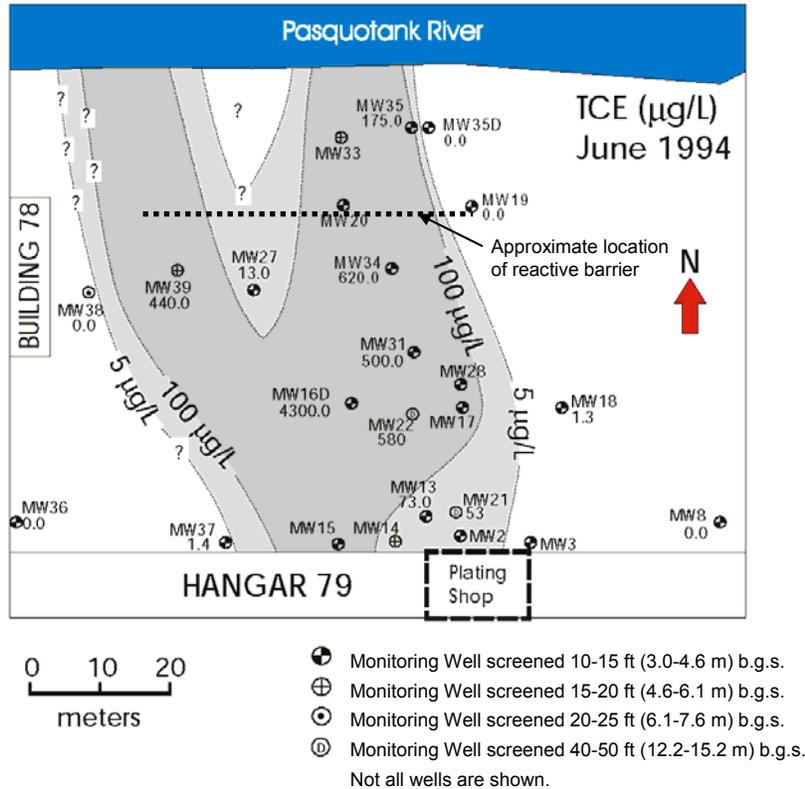


Figure 3. Site map showing TCE plume based on data from June 1994 and approximate location of permeable reactive barrier (modified from Blowes et al., 1999a).

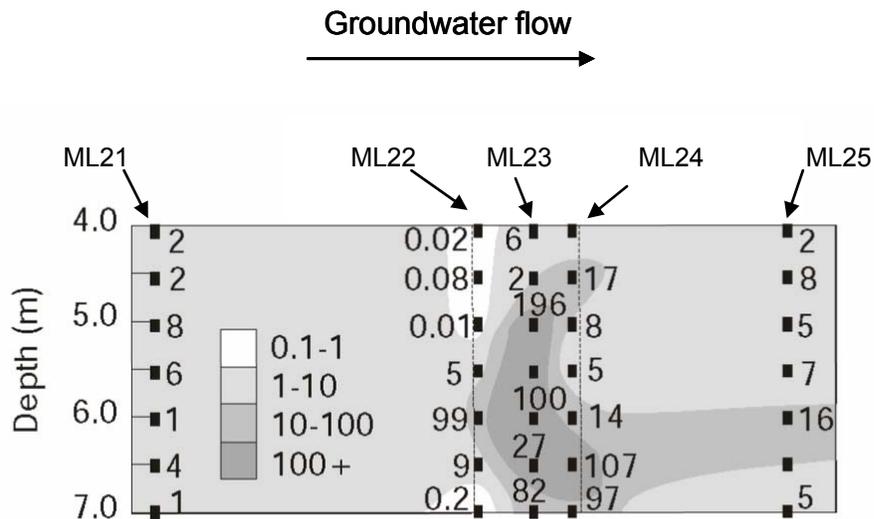
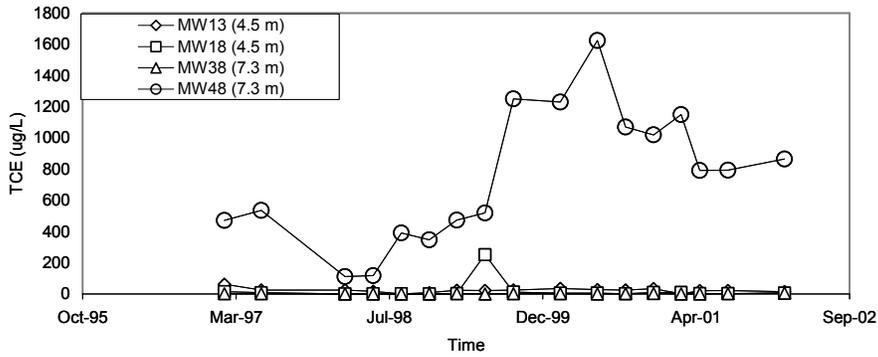
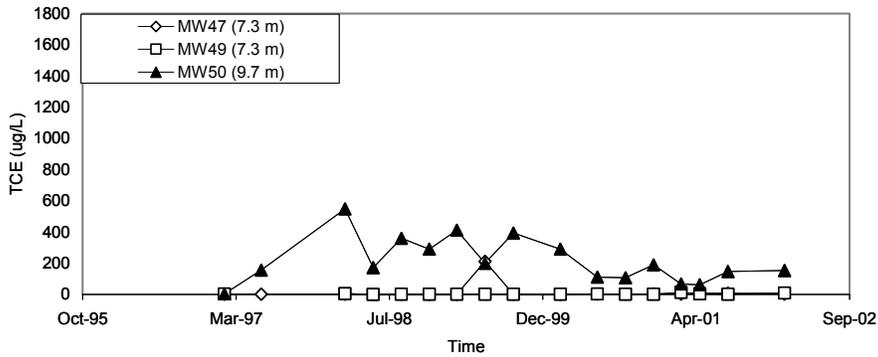


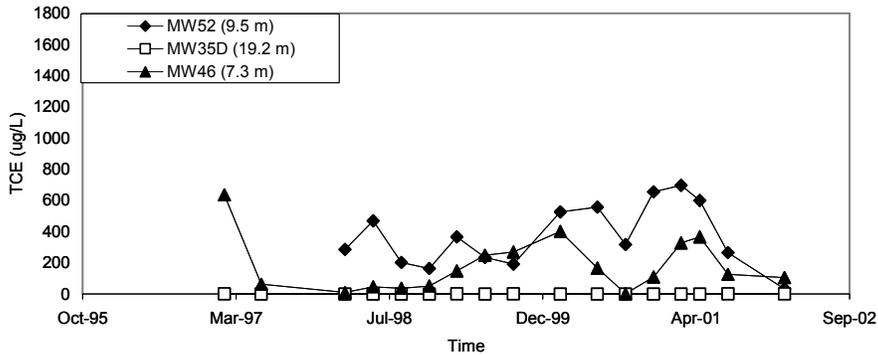
Figure 4. Distribution of hydraulic conductivities (m/day) measured using slug testing in multilevel samplers from transect 2 ~6 months after the PRB was installed (modified from Blowes et al., 1999b). Refer to Figure 2 for transect location within the PRB.



(a)



(b)



(c)

Figure 5. TCE concentrations in groundwater monitoring wells located upgradient (a), ~2 m downgradient (b), and near the Pasquotank River (c). Well depth shown in parentheses in legend. Data obtained from Paul et al., 2003.

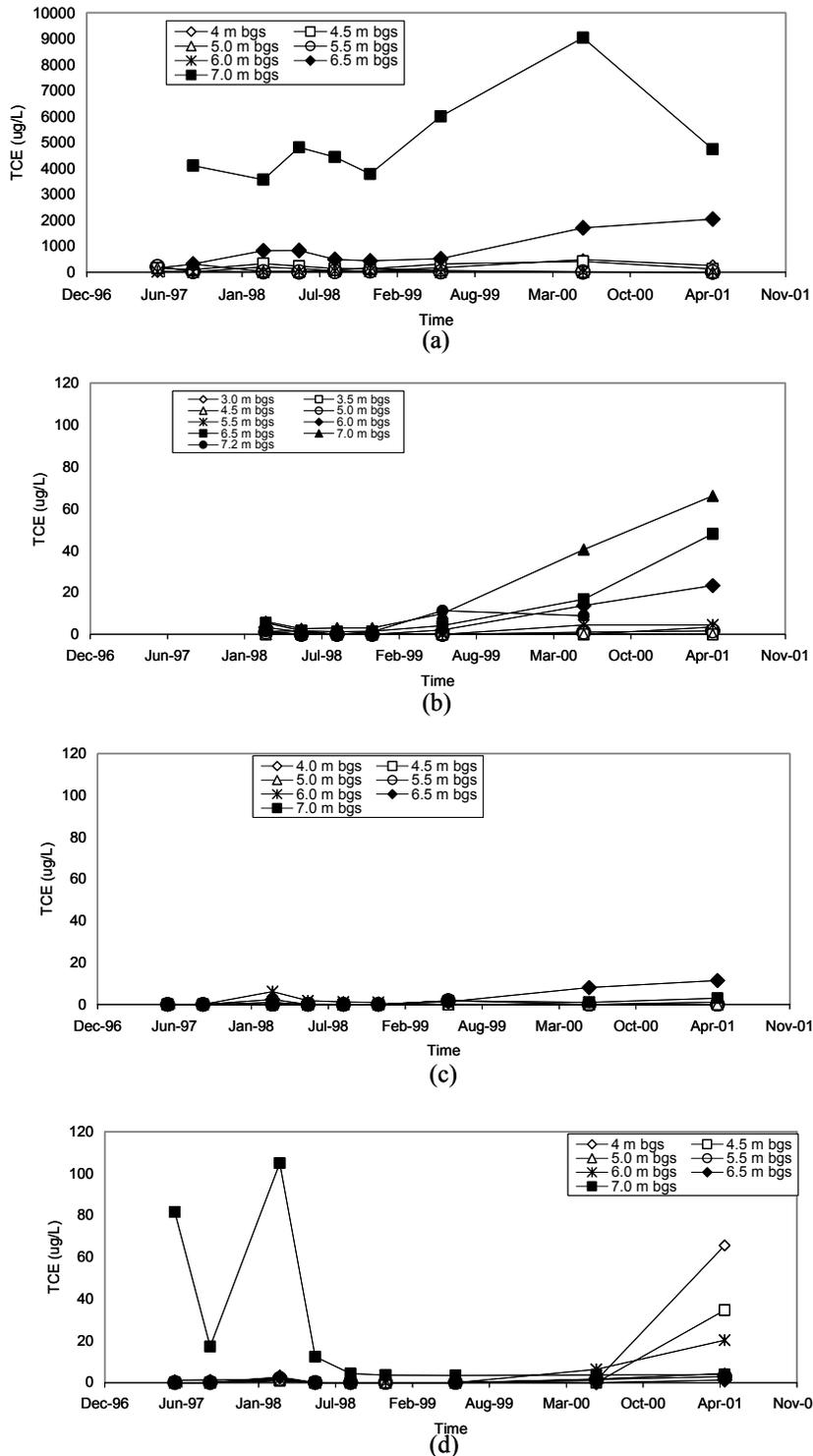
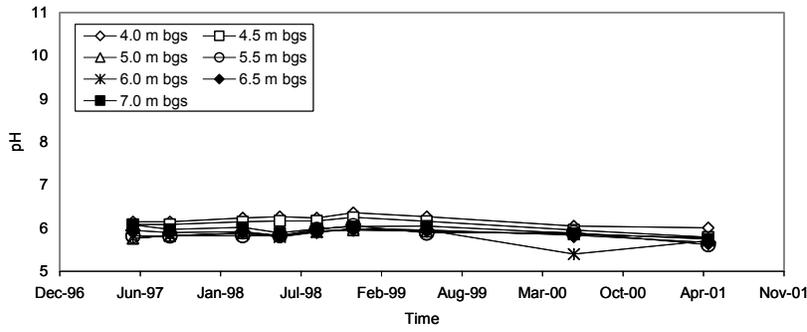
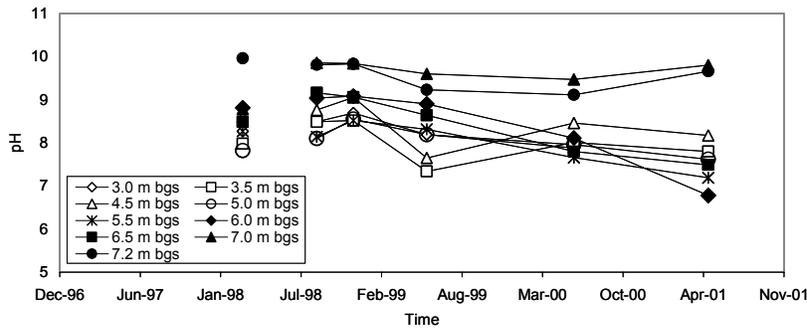


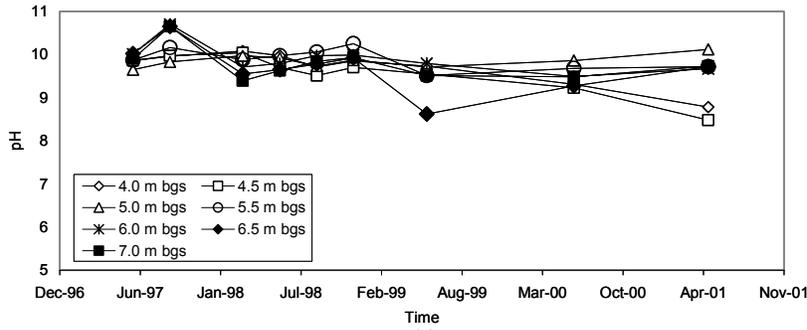
Figure 6. TCE concentrations in multilevel samplers: (a) ML21 ~2 m upgradient of the barrier, (b) ML23.5 in the upgradient aquifer/PRB fringe, (c) ML24 in the PRB, and (d) ML25 ~1.5 m downgradient of the PRB. Note that the vertical scale in (a) is different from the vertical scales in (b)-(d). Legend shows sampler depth. Data obtained from Paul et al., 2003.



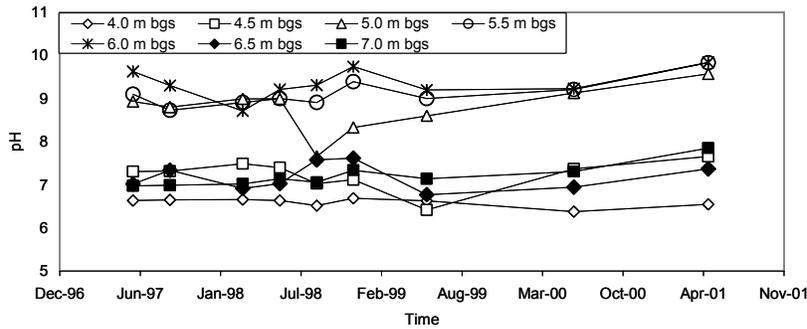
(a)



(b)



(c)



(d)

Figure 7. pH in multilevel samplers: (a) ML21 ~2 m upgradient of the barrier, (b) ML23.5 in the upgradient aquifer/PRB fringe, (c) ML24 in the PRB, and (d) ML25 ~1.5 m downgradient of the PRB. Legend shows sampler depth. Data obtained from Paul et al., 2003.

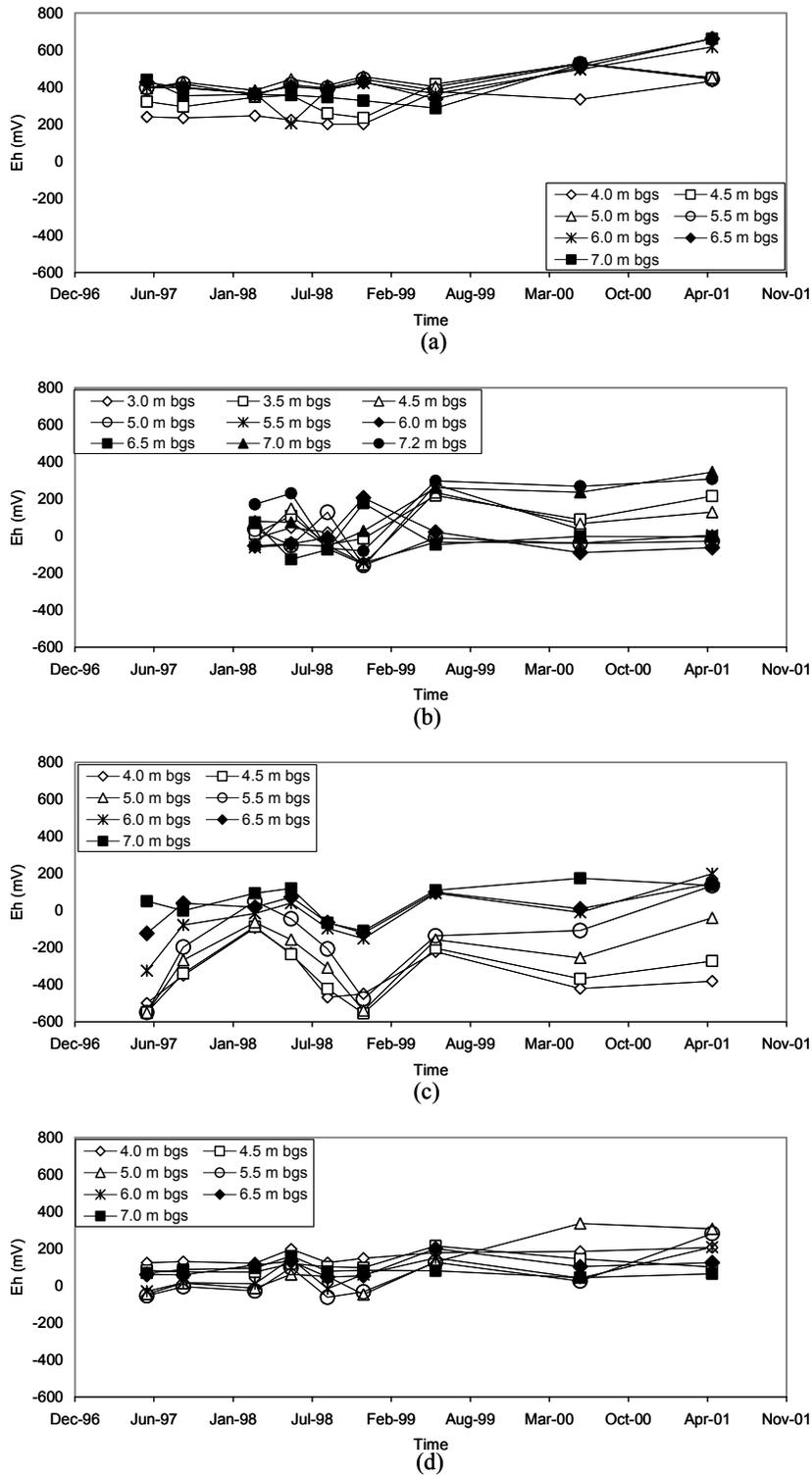


Figure 8. Eh in multilevel samplers: (a) ML21 ~2 m upgradient of the barrier, (b) ML23.5 in the upgradient aquifer/PRB fringe, (c) ML24 in the PRB, and (d) ML25 ~1.5 m downgradient of the PRB. Legend shows sampler depth. Data obtained from Paul et al., 2003.

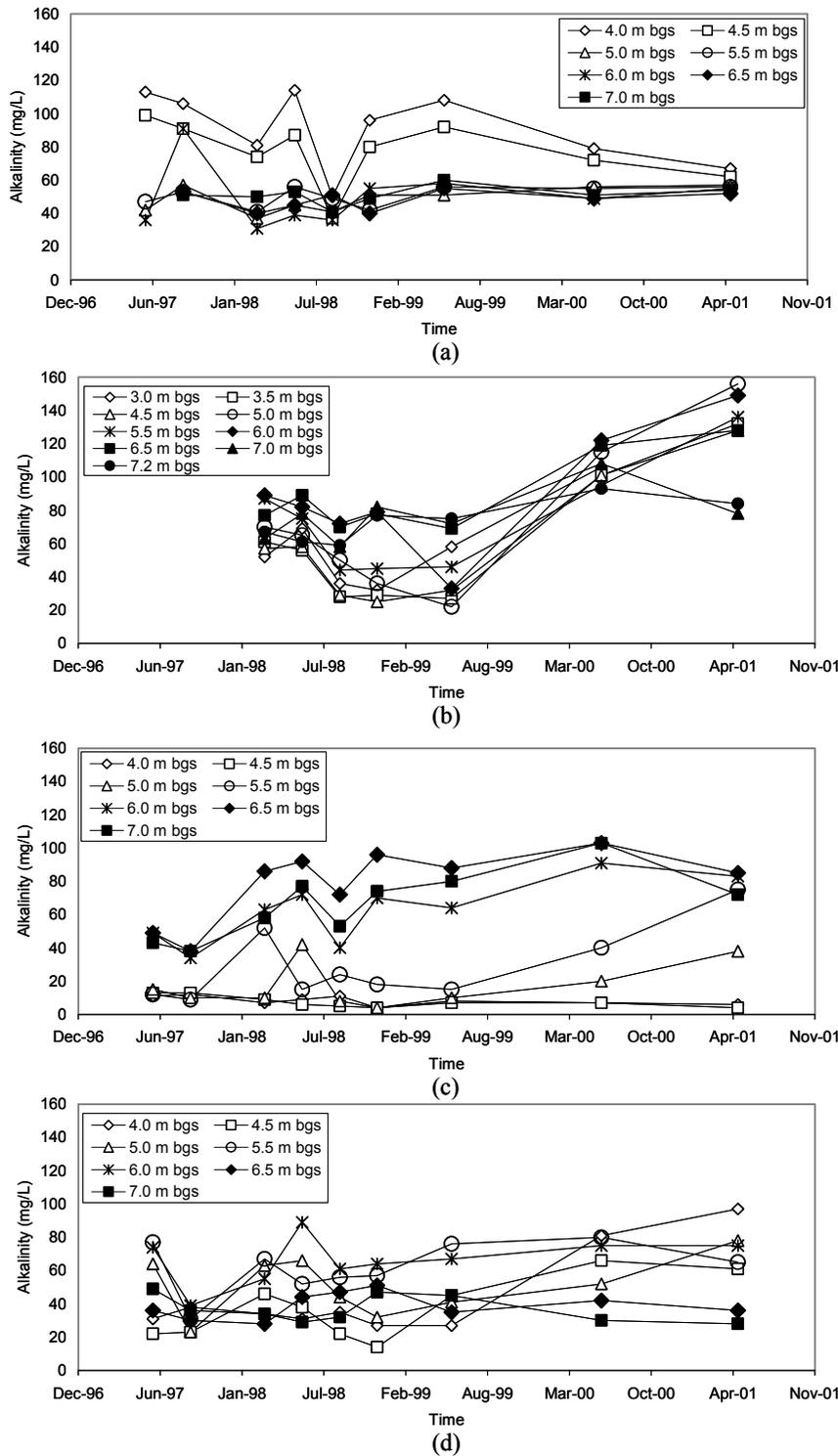


Figure 9. Alkalinity (mg/L) in multilevel samplers: (a) ML21 ~2 m upgradient of the barrier, (b) ML23.5 in the upgradient aquifer/PRB fringe, (c) ML24 in the PRB, and (d) ML25 ~1.5 m downgradient of the PRB. Legend shows sampler depth. Data obtained from Paul et al., 2003.

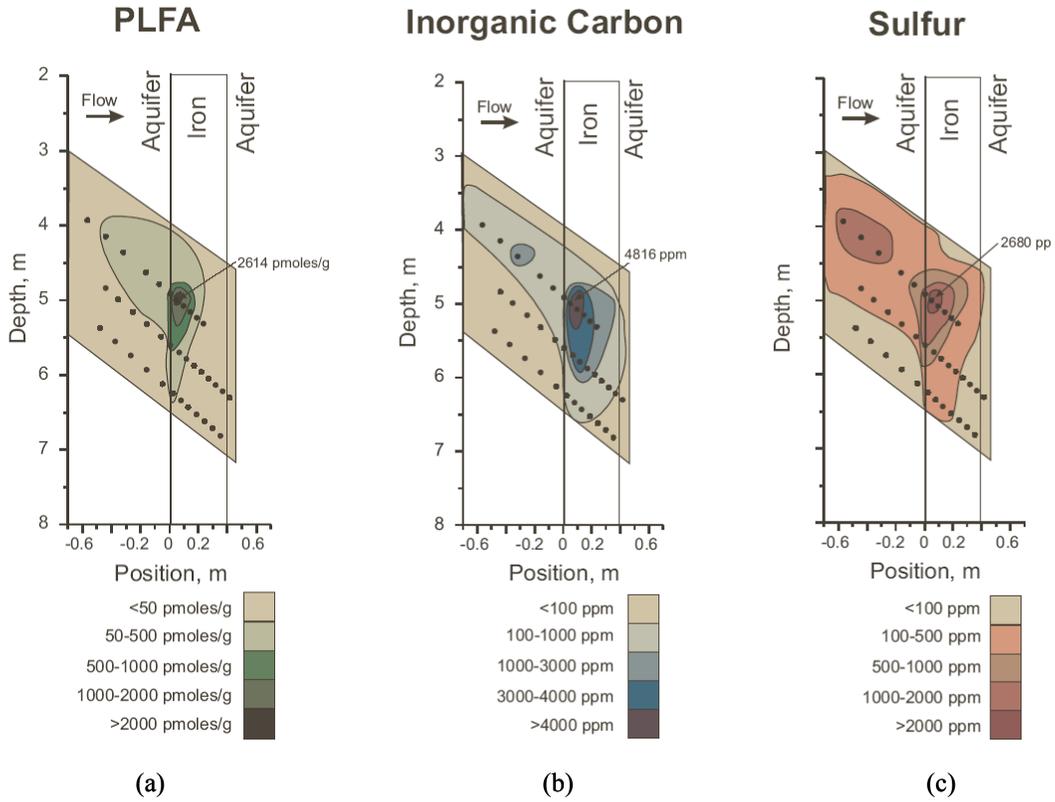


Figure 10. Results of solid phase analysis of cores collected from the PRB in 2000. (a) Biomass from phospholipid fatty acid analysis (PLFA), (b) inorganic carbon, (c) sulfur. Figures from Wilkin et al., 2003.

Table 1. Minimum and maximum values for selected parameters in multi-level samplers along transect 2 (see Fig. 2 for location of transect and sampling locations) measured in May 2001 approximately 5 years after PRB installation.

	Sampling Locations			
	ML21 ~2 m upgradient of PRB 4.0-7.0 m bgs	ML23.5 Upgradient aquifer/PRB interface 3.0-7.2 m bgs	ML24 Within PRB 4.0-7.0 m bgs	ML25 ~1.5 m downgradient of PRB 4.0-7.0 m bgs
	Hexavalent Chromium (mg/L)			
Minimum	N.D.	N.D.	N.D.	N.D.
Maximum	1.9	N.D.	N.D.	N.D.
	Trichloroethylene (µg/L)			
Minimum	N.D.	N.D.	N.D.	2.9
Maximum	9040	66.2	11.4	65.6
	cis-1,2-Dichloroethylene (µg/L)			
Minimum	N.D.	N.D.	N.D.	N.D.
Maximum	206	298	18	74.6
	Vinyl Chloride (µg/L)			
Minimum	N.D.	N.D.	N.D.	N.D.
Maximum	26.8	35.3	31.1	N.D.
	Ethane (µg/L)			
Minimum	N.D.	2	N.D.	N.D.
Maximum	N.D.	35	12.9	16.9
	Ethene (µg/L)			
Minimum	N.D.	3	3	N.D.
Maximum	N.D.	43	10.7	13.6
	Methane (µg/L)			
Minimum	16	67	959	245
Maximum	98	5304	4049	4515

^aExtrema for each multi-level sampler were obtained from data sets in Paul et al. 2003. Each set includes data from all sampling depths (3-7.2 m for ML23.5, 4-7 m from the others) and all sampling events (1997-2001). Maximum and minimum values shown for methane are from Feb 1997 when methane measurements were last performed (Blowes et al., 1999b).

Table 2. Minimum and maximum values for selected parameters in multi-level samplers along transect 2 (see Fig. 2 for location of transect and sampling locations) measured in May 2001 approximately 5 years after PRB installation.

Description	Sampling Locations			
	ML21 ~2 m upgradient of PRB	ML23.5 Upgradient aquifer/PRB interface	ML24 Within PRB	ML25 ~1.5 m downgradient of PRB
Sampling Depths	4.0-7.0 m bgs	3.0-7.2 m bgs	4.0-7.0 m bgs	4.0-7.0 m bgs
	pH			
Minimum	5.4	6.8	8.5	6.38
Maximum	6.4	10.0	10.7	9.84
	Eh (mV)			
Minimum	199	-165	-554	-63
Maximum	660	343	200	335
	Sulfate (mg/L)			
Minimum	23.4	<1.0	<1.0	<1.0
Maximum	91.5	3.22	<1.0	17.8
	Nitrate + Nitrite (mg/L)			
Minimum	<0.1	<0.1	<0.1	<0.1
Maximum	1.49	<0.1	<0.1	<0.1
	Alkalinity (mg/L)			
Minimum	31	22	4	14
Maximum	114	156	103	97
	Ferrous Iron (mg/L)			
Minimum	N.D.	N.D.	N.D.	N.D.
Maximum		6.8	0.93	2.04
	Specific Conductivity (μS/cm)			
Minimum	42	62	42	86.5
Maximum	807	397	342	442

^aExtrema for each multi-level sampler were obtained from data sets in Paul et al. 2003. Each set includes data from all sampling depths (3-7.2 m for ML23.5, 4-7m from the others) and all sampling events (1997-2001).

Full-Scale Mulch Biowall at Offutt Air Force Base (AFB), Nebraska

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1.0 SITE DESCRIPTION AND HISTORY

Offutt AFB is located in eastern Nebraska approximately five miles south of the city of Omaha (Figure 1). The site has been a military installation since 1894 and with the merging of several military facilities in 1948, Offutt AFB was formed. Its modern history as an important site of aircraft manufacturing began in 1942. From 1941 through 1965, Building 301 served as the site of the Martin Bomber Building Plant and was used for various operations including manufacturing military aircraft, packaging, shipping aircraft, and guided missile assembly. From 1941 to 1946 the southwest part of the building was used as a chemical laboratory and cleaning and plating room (including an acid pit) among other operations. These activities are believed to be the sources of trichloroethene (TCE) contamination found in a groundwater plume emanating from the vicinity of Building 301.

In 1999, the Air Force Center for Environmental Excellence (AFCEE) initiated a cooperative program with the Offutt AFB Environmental Remediation Program (ERP) to test several innovative groundwater treatment technologies to address contamination by chlorinated volatile organic compounds (cVOCs) at the site. These activities include deployment and testing of both pilot-scale and full-scale permeable biological reactive barriers (biowalls) that used a mulch-sand mixture as the reactive medium. The pilot-scale biowall was installed in January 1999 followed by emplacement of a full-scale biowall in July 2001.

Figure 2 is an aerial photograph of part of Offutt AFB showing the location of Building 301. Isoleths defining the TCE plume also are illustrated along with the location of cross section AA'. The plume configuration is based on data obtained in spring 2000, more than one-year after a pilot-scale biowall had been installed at the site. The approximate locations of the biowalls also are identified in Figure 2.

This case study focuses on the full-scale biowall and associated performance monitoring that occurred between 2001 and 2003. The information contained in this case study comes from a report prepared for AFCEE by Groundwater Services, Inc. (GSI, 2004). Greater detail about the full-scale biowall including tabulation of all performance monitoring data can be obtained from this report. A summary of cost and performance information for the pilot-scale wall is reported in AFCEE (2003).

2.0 GEOLOGIC AND HYDROLOGIC CHARACTERISTICS OF THE SITE

The main part of Offutt AFB is located on a dissected alluvial terrace of Pleistocene age that is a remnant geomorphologic feature associated with the nearby Missouri River. Figure 3 is a cross section (AA') through the site that extends westward from Building 301 approximately 3600 ft (1100 m). The ground surface slopes downward to the west of the building from an elevation of approximately 1060 ft above mean sea level (amsl) to 975 ft amsl at the western margin of the cross section. In the vicinity of Building 301, in addition to some surficial fill material, the terrace is underlain by a sequence of lithologies of glacial origin including loess and several outwash units that overlie an extensive layer of till. These units transition westward into relatively thick sandy/silty alluvial deposits.

Underlying Building 301 the groundwater table occurs at a depth of approximately 45 ft below ground surface (bgs). The water table slopes westward and lies at a depth of only 3-10 ft bgs at the western margin of cross section AA'. The direction of shallow groundwater flow in the vicinity of the cross section is generally to the west. An estimate of the hydraulic conductivity of the upper alluvial clay and silt unit from a location near the biowall in cross section AA' (MW-9S: see Figure 4 for location) was obtained from the mean of five slug tests and yielded a result of 3.5 ft/day (1.2×10^{-3} cm/sec). This mean value of hydraulic conductivity coupled with estimates of effective porosity (0.15) and hydraulic gradient (0.01) yields a shallow groundwater velocity of 0.23 ft/day (85 ft/yr), a value that is assumed to be relevant to the area around the biowall.

3.0 NATURE AND EXTENT OF CONTAMINATION (PRE-ENHANCEMENT)

As noted above, activities associated with Building 301 from 1941 to 1946 apparently are responsible for the leaking of cVOC contaminants (mainly TCE) to the subsurface. Since its release to the subsurface, contamination has migrated downward more than 40 ft to the water table and created a dissolved phase plume that extends over 3000 ft to the west. As illustrated in Figure 3, this plume is confined to a zone in approximately the upper 20 ft of the alluvial clay and silt in the vicinity of the biowall.

The highest concentrations of dissolved TCE in groundwater are found underlying Building 301 and exceed 10 mg/L (spring 2000). This concentration is approximately 1% of the aqueous solubility of TCE and is a level that frequently is cited as evidence for the likely presence of DNAPL nearby. Dissolved concentrations of TCE as high as 1200 µg/L have been observed down gradient of the source near the location of the biowalls (spring 2000).

4.0 APPLICATION OF THE ENHANCEMENT

In January, 1999, AFCEE, in association with the ERP at Offutt AFB, installed a pilot-scale mulch biowall that intersected a portion of the plume illustrated in Figure 3 (see Figures 3 and 4 for location). This pilot-scale biowall is 100 ft long, 1 ft thick, and extended to a total depth of 23 ft in a trench excavated by conventional trenching machinery. The selection of an organic mulch material as a reactive medium was based on observations that active reductive dechlorination of cVOCs was occurring underlying a nearby agricultural field. It was concluded that the high concentration of natural organic matter in the soil served as an effective electron donor and created a favorable environment for anaerobic degradation of TCE and its chlorinated daughter compounds to innocuous byproducts. In addition, the low cost of the mulch medium was an important factor in the decision because it consisted of shredded trees and leaves generated on-site, mixed with sand in a 1:1 volume ratio. It was an attractive alternative to other, more costly types of reactive media such as zero valent iron. The goal of the pilot project was to evaluate the cost and performance factors of the biowall concept to ascertain if a full-scale application was warranted.

The conceptual framework for the pilot-scale biowall is described in the project summary as follows:

“This treatment method relies on the flow of groundwater under a natural hydraulic gradient through the biowall to promote contact with slowly-dissolving organic matter. Degradation of the substrate by microbial processes in the subsurface provides a number of breakdown products, including metabolic acids... [that] provide secondary electron donors or fermentable substrates for hydrogen generation, the primary electron donor used in reductive dechlorination. During reductive dechlorination, TCE is sequentially reduced to cis-1,2-dichloroethene (DCE), vinyl chloride, and ethene.” (AFCEE, 2003)

During the first 31 months of operation of the pilot-scale biowall, groundwater chemistry data within and down gradient of the wall indicated declines of dissolved oxygen (DO), nitrate, and sulfate and production of methane, all of which are indicators that a reducing environment was established. The removal of TCE over this time period was variable, but averaged 70% with no accumulation of vinyl chloride (VC). These results are summarized in AFCEE (2003).

On the strength of the initial results for the pilot-scale biowall, a full-scale mulch biowall was installed at the same site in July 2001, approximately 30-40 ft to the east of the original biowall (Figure 4). The full-scale biowall used a mulch-sand mixture with 50% by volume of each component. The biowall is 500 ft long, 25 ft deep, and 1.5 ft thick and was emplaced by using continuous trenching methods. At its northern end the full-scale wall overlaps the pilot-scale wall. Figure 4 also illustrates that the full-scale wall crosses both a buried gas main and storm sewer. During construction the storm sewer was excavated, dismantled in the vicinity of the biowall to permit construction of a continuous wall, and then reconnected. For safety reasons, at the location of the gas main the wall was completed with a gap. The gap provides an opportunity for groundwater to bypass the mulch medium in this location and not undergo treatment.

A network of monitoring wells had been constructed to evaluate the performance of the pilot-scale biowall and was augmented by a series of new wells constructed in association with the full-scale wall (Figure 4). Included in this latter phase of well construction were five wells completed within the biowall itself. The monitoring wells were completed to a nominal depth of 20 ft with a 10-ft screen between 10-20 ft bgs. Performance evaluation of the full-scale biowall began with groundwater sampling in July 2001, shortly after the wall was installed. Additional sampling occurred quarterly over the next two years with the final sampling taking place in July 2003. Another round of samples will be collected in the summer of 2006 as part of a follow-on monitoring effort to evaluate the sustainability and long-term performance of the biowall.

5.0 IMPACT OF ENHANCEMENT ON MEASURABLE PROPERTIES OF THE SYSTEM

5.1 Monitoring facilities

As noted, Figure 4 illustrates the location of both the pilot- and full-scale biowalls, monitoring wells, and other features of the site. In addition, isopleths for TCE concentrations showing the configuration of the contaminant plume in groundwater also are provided. The contours are based on data obtained in the spring of 2000, more than one-year after construction of the pilot-scale wall and more than a year prior to installation of the full-scale wall.

Figure 5 focuses on the northern part of the full-scale biowall. Three transects of monitoring wells are identified in this region that are examined in detail in this case study for information related to the performance of the biowalls. These transects were chosen because they permit evaluation of the impact of the full-scale biowall alone (Transects B and C) and the coupled impact of both biowalls (Transect A) on groundwater contamination. Other transects (Figure 4) have been excluded from evaluation in this case study because: a) the transect of wells to the north of Transect A appears to show evidence of groundwater flow (and contaminant transport) around the north end of the biowalls and b) the inferred direction of groundwater flow in the southern section of the full-scale biowall (i.e. to the south of Transect C) indicates that flow is to the North in this region and parallel to the wall, with little or no flow through the biowall. In contrast, water level data for the northern section of the biowall, as illustrated in Figure 5, indicate that the direction of groundwater flow in this region is more nearly normal to the wall. These factors are discussed further in AFCEE (2004).

An important initial step in the evaluation of treatment of groundwater by the biowall at Offutt AFB is to consider the time-variability of contaminant concentrations in the plume approaching the biowall. This will help distinguish between natural compositional fluctuations of the plume and those changes within a transect that can be ascribed to the impact of the biowall. Another factor to consider is the timing of groundwater sampling relative to the location of monitoring wells, the time of installation of the biowall, and the velocity of groundwater. This assessment determines if sufficient time has elapsed since emplacement of the biowall for treated groundwater to have reached the wells.

Groundwater monitoring conducted in spring 2000 as well as between July 2001 and July 2003 associated with performance evaluation of the full-scale wall confirms that the location of the most contaminated part of the plume lies in the vicinity of MW-45S and MW-46S (Figure 5) and remains relatively unchanged over the period from spring 2000 to 2003. However, evidence suggests some minor North to South migration of the plume axis occurs that leads to temporal variability of TCE concentrations in these and other wells in the general vicinity. In addition, one cannot rule out the possibility that some fluctuation in concentrations in these two wells over time are the result of temporal variability in the upgradient source term and/or other factors that control downgradient concentrations of TCE in the plume. Examples of the temporal variability of TCE concentrations is provided by the four wells that are upgradient of the full-scale biowall (*i.e.*, not impacted by either the pilot-scale or full-scale walls). Data reported in GSI (2004) illustrates that TCE concentrations in MW-22S, MW-27S, MW-45S, and MW-46S (Figure 5) varied over a range by factors of from three to five (within each well) between July 2001 and July 2003. A similar effect was observed during performance monitoring of the pilot-scale wall (AFCEE, 2004). Temporal variability of contaminant concentrations in groundwater in the plume has to be considered when trying to separate this effect from changes due to the impact of the biowalls.

When evaluating the impact of the biowalls on groundwater contamination from the various monitoring wells illustrated in Figure 5, it is important to consider their location relative to that of the biowalls, the time of sampling of the wells (from July 2001 – July 2003) in comparison to the date of biowall installation (pilot-scale wall: January 1999; full-scale wall: July 2001) and the estimated velocity of groundwater flow (85 ft/yr). First, as mentioned, one must assume that groundwater collected from the upgradient wells (MW-45S, MW-46S, MW-22S, and MW-27S) are not impacted by the biowalls. Secondly, groundwater from wells emplaced within the biowall (*e.g.* BW-1 and BW-2) may show a rapid response to the mulch following installation. Third, none of the wells downgradient of the full-scale biowall (MW-23S, MW-24S, and all down gradient wells in Transect B and C) are likely to see any impact from this biowall during the July 2001 sampling period (immediately following emplacement of the biowall) as treated groundwater would not have sufficient time to reach any of these wells at the estimated velocity of 85 ft/yr. However, as anticipated for the July 2002 and subsequent sampling events, all of the downgradient wells should show the influence of treatment by the biowall as they are located within 85 ft of the biowall.

5.2 Monitoring results

There are two principal ways of evaluating the performance of a biowall. First, the biowall should be assessed for its ability to create a chemical environment favorable for the reductive dechlorination of TCE. Second, objective evidence should be present for the degradation of TCE as contaminated groundwater passes through the biowall, coupled with increases in the concentration of key degradation products (*e.g.*, lesser chlorinated ethenes, methane, etc.). Although analytical results for a broad range of cVOC analytes are available for groundwater from this site, the following evaluation will focus on relative changes in the concentrations of the parent contaminant (TCE) and the terminal products from reductive dechlorination (ethene and ethane).

As discussed in AFCEE (2004), a variety of chemical parameters were measured in the monitoring wells to assess whether the environment created by the biowall was favorable to the anaerobic bacteria believed to be responsible for reductive dechlorination of TCE. The list of parameters measured included alternative electron acceptors (*e.g.*, DO, nitrate, sulfate) and indicators of redox state (*e.g.*, ferrous iron, methane, redox potential). In summary, DO, nitrate, and sulfate concentrations in groundwater decreased upon passage through the biowall. In contrast, the concentrations of ferrous iron and dissolved methane increased. All of these observations confirm that the biowall is effective in creating a reducing environment and in removing alternative electron acceptors that would compete with reductive dechlorination of TCE. A more detailed analysis of the changes in these parameters, including the relevant analytical data, is found in AFCEE (2004).

The most direct line of enquiry for evaluating the impact of the biowall on dissolved cVOC contaminants in groundwater comes from an assessment of evidence related to reductive dechlorination of TCE (*i.e.*, a decline in its concentration) and increases in the concentration of daughter products. Figures 6a, 6b, and 6c illustrate changes in concentration of TCE for transects A, B, and C across the biowalls. The relative locations of the biowalls within these transects are indicated. Data for sampling dates in July for 2001, 2002, and 2003 are included. However, as noted above, only the samples collected in July 2002 and July 2003 from monitoring wells located downgradient of the full-scale biowall contain groundwater that has passed through that wall. Groundwater samples down gradient from the pilot-scale wall in Transect A have been impacted by that biowall for the July 2001 sampling period because the wall was installed in January 1999, over two years earlier. In general, the concentration of TCE in groundwater is seen to decline across both biowalls for all three sampling periods in each transect. The declining trend across the full-scale biowall for July 2001, prior to when the wall could have had any impact, probably reflects natural temporal variations in groundwater composition unrelated to the presence of the biowall. In Transect A it is significant to observe that both the full-scale and pilot-scale biowalls appear to have enhanced removal of TCE from groundwater.

In order to evaluate contaminant concentrations within the transects, whatever the cause(s), comparisons of the TCE concentrations immediately upgradient and downgradient of the biowalls can be made. Comparison among the results for July 2001, where there should be no impact from the biowall, and July 2002/July 2003, where evidence of reductive dechlorination should exist, will permit an opportunity to distinguish those variations in composition related to the influence of the biowalls. Table 1 contains this comparison for well pairs in the three transects by normalizing the downgradient concentration of TCE to that in the upgradient well. Therefore, for July 2001 (before the downgradient wells could be impacted by the full-scale biowall) it is observed that TCE_D/TCE_U ranges between 0.31 and 1.3 for the three transects. This range presumably represents the range of natural temporal variations for the plume in this area. In contrast, comparison of TCE concentrations in well pairs where the biowalls are expected to have had an impact on groundwater show dramatically different results. The normalized ratio for MW-23S (downgradient) to MW31S (upgradient) for the pilot-scale wall is 0.0091 for July 2001. Furthermore, for both the pilot-scale and full-scale biowalls in the three transects, the normalized ratio of TCE varies from 0.0052 to 0.39 for July 2002 and from 0.0014 to 0.15 for July 2003. These results clearly indicate that TCE is being removed from groundwater as it passes through both biowalls for the three transects. Indeed, comparison of the ratios for impacted versus non-impacted groundwater suggest typical removal efficiencies for TCE of from 60% to >90% due to treatment by the biowall.

The mechanism believed to be responsible for degradation of TCE by the biowalls (*i.e.*, reductive dechlorination) offers another way to evaluate its impact on groundwater. TCE will sequentially degrade

into cis 1,2-DCE, VC, ethene and ethane⁵. Therefore, as water contaminated with TCE enters the biowall, cis-1,2-DCE should first accumulate and then be degraded to VC and, ultimately, to ethene and ethane. In a perfectly efficient biowall all of the parent TCE and intermediates (cis 1,2-DCE and VC) should be degraded with only ethene and ethane being released downgradient. Consequently, one measure of how well the wall is performing can be ascertained by evaluating the molar ratio of the ultimate daughter degradation products (ethene + ethane) to the parent compound (TCE) which should show a declining trend within each transect if the biowalls are having the expected impact. Figures 6a, 6b, and 6c present information on changes in the molar ratio of ethene + ethane to TCE for the three transects. Groundwater from those monitoring wells that bracket the biowalls in each transect have an increase in the ethene + ethane:TCE ratio in a down gradient direction. However, a general increase in this ratio is observed also for those well pairs across the full-scale biowall for the July 2001 sampling period which, as noted above, occurred too soon after installation of the wall to impact groundwater composition. Therefore, as for TCE concentrations, it is useful to extend this analysis in an attempt to distinguish between natural temporal variations in plume chemistry and evidence of significant in-growth of ethene.

In the same manner as for TCE it is helpful to normalize the molar ratio of ethene + ethane to TCE in wells immediately downgradient of the biowall with that in the paired up gradient wells. These results are provided in Table 1. First, pre-construction results (July 2001) for the full-scale biowall yield values for the ratio $([\text{ethene}+\text{ethane}]/\text{TCE})_D/([\text{ethene}+\text{ethane}]/\text{TCE})_U$ that range from 0.68 to 4.7. The same ratio for the wells bracketing the pilot-scale wall for July 2001 is 44,200, a value that indicates a significant relative enrichment of ethene and ethane due to the impact of the biowall. Groundwater from the July 2002 and July 2003 sampling periods has one value of the ratio of 1.1 (Transect C) with the four other values falling within a range between 38 and 11,850. Consequently, it is apparent that the biowalls result in a one to four-order of magnitude increase of ethene + ethane relative to TCE.

5.3 Other factors

Attempts have been made in GSI (2004) to compute a mass balance of parent and daughter products entering and leaving the biowall. TCE, cis 1,2-DCE, VC, ethene and ethane were considered in this analysis. The apparent mass balance can only account for approximately 25% of the contaminants entering the biowall from up gradient. However, the effects of temporal variations of the concentration of TCE entering the biowall could not be evaluated and, as discussed, occur and may impact the apparent mass balance results. Furthermore, it is acknowledged that other reaction pathways leading to byproducts that were not evaluated in this analysis could be a factor in the mass balance results. Finally, the effects of sorption need to be considered.

Because the biowall is a large reservoir of organic carbon, it is possible that some apparent removal of TCE is the result of sorption rather than reductive dechlorination. This possibility is evaluated in GSI (2004) where it is concluded that within one year following emplacement of the biowall a steady state condition involving sorption would be achieved such that it would no longer be an effective removal mechanism.

Although the impact of the biowalls might be best approached by assessing changes in the mass flux of TCE and its degradation products, available information does not permit this type of evaluation. The monitoring network does not include a detailed network of multilevel sampling points or deployment of flux monitors such as those described by Hatfield, et al. (2004) to evaluate the contaminant flux at

⁵ Monitoring data presented in GSI (2004) establish that there is little or no accumulation of VC in groundwater due to the full-scale biowall. This effect also was observed and reported for the pilot-scale wall (AFCEE, 2003)

different times. Therefore, the more general, semi-quantitative approach presented here estimates the impact of the biowall through the apparent removal of TCE and in-growth of ethene over the time interval of monitoring.

5.4 Sustainability of the enhancement

There are two components to the issue of sustainability of a biowall: a) effectiveness of reductive dechlorination of TCE over time and b) changes of the hydraulic properties of the biowall. The results presented in Table 1 along with the more extensive data provided in GSI (2004) suggest that the pilot-scale and full-scale biowalls have been effective in promoting reductive dechlorination during the two years from July 2001 to July 2003. It is not apparent that any significant diminution of effectiveness has occurred. In fact, in terms of the relative production of ethene and ethane, available data seem to suggest a comparable level of effectiveness over this time period (Table 1).

Beginning in July 2001, shortly after installation of the full-scale biowall, rising head slug tests were performed on the five wells located within the biowall. These tests were repeated annually through July 2003 and all results are reported in GSI (2004). Figure 7 illustrates the results and establishes that over the two-year period of measurement a decline in hydraulic conductivity by a factor of 3 to 5 occurred. As noted in the figure, the initial hydraulic conductivity of the biowall was comparable to that of the aquifer, but by July 2003 the biowall was clearly less permeable than the aquifer. This trend is of concern because it increases the probability that contaminated groundwater will flow around the biowall rather than through it as the differential in conductivity increases. This is both a sustainability and a design issue that has been addressed in biowalls subsequent to those installed at Offutt AFB. As noted in GSI (2004), the specific cause of the decline has not been determined although settling or fouling of the medium are the most likely explanations.

6.0 SUMMARY AND CONCLUSIONS

The main goal of the two biowalls installed at Offutt AFB, NE, was to evaluate the efficacy of mulch to promote the reductive dechlorination of TCE and its daughter products, cis-1,2-DCE and VC. The mulch served as an organic substrate to create anaerobic conditions in the aquifer. Once anaerobic conditions were achieved, fermentation of soluble organic substrates derived from the mulch produced hydrogen, which served as the primary electron donor for reductive dechlorination. Comparison of the ratios for impacted versus non-impacted groundwater at the site suggest typical removal efficiencies for TCE of from 60% to >90% due to treatment by the biowall. Sustained performance of the biowall appears to be viable for at least 36 months of operation without the requirement for recharging of the carbon substrate.

AFCEE and its partners are actively investigating the sustainability and long-term performance of biowalls. As of this writing, the US Air Force has installed eight biowalls. In the summer of 2006, AFCEE will revisit two of its older biowall systems to evaluate the degradation processes that occur (both biotic and abiotic) within biowalls, determine the sustainability of these degradation processes over time, and identify ways to optimize performance of mulch biowalls. To date, little is known on the long-term effectiveness of mulch biowalls and the minimum or threshold concentrations of mulch and compost substrate that are required to sustain anaerobic degradation. The results of the summer 2006 sampling and analysis, as well as the release of biowall protocol, can assist those by providing design/monitoring issues that ought to be considered if a biowall is being considered as an enhancement. An additional source of such information can be found in the *Principles and Practices of Enhanced Anaerobic Bioremediation of Chlorinated Solvents* (AFCEE, 2004).

7.0 REFERENCES

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Table 1. Molar ratios illustrating TCE degradation and ethene + ethane production in down gradient (D) versus up gradient (U) monitoring wells. See Figure 5 for location of well pairs. Values in bold italics were obtained too soon after construction of the full-scale biowall to be influenced by it.

Well Pairs (D / U)	Full (F) - or Pilot(P)- Scale Biowall	July 2001		July 2002		July 2003	
		TCE _D /TCE _U	(Ethene+Ethane)/TCE _D (Ethene+Ethane)/TCE _U	TCE _D /TCE _U	(Ethene+Ethane)/TCE _D (Ethene+Ethane)/TCE _U	TCE _D /TCE _U	(Ethene+Ethane)/TCE _D (Ethene+Ethane)/TCE _U
<u>Transect A:</u>							
MW-23S/MW-46S	F	<i>0.31</i>	<i>4.7</i>	0.12	3260	0.038	3320
MW-31S/MW-23S	P	0.0091	44,200	0.011	-	<0.083	-
<u>Transect B:</u>							
MW-47S/MW-22S	F	<i>0.57</i>	<i>5.7</i>	0.0052	11,850	0.0014	6080
<u>Transect C:</u>							
MW-48S/MW27S	F	<i>1.3</i>	<i>0.68</i>	0.39	1.1	0.15	38



Figure 1. Location map for Offutt AFB, Nebraska.

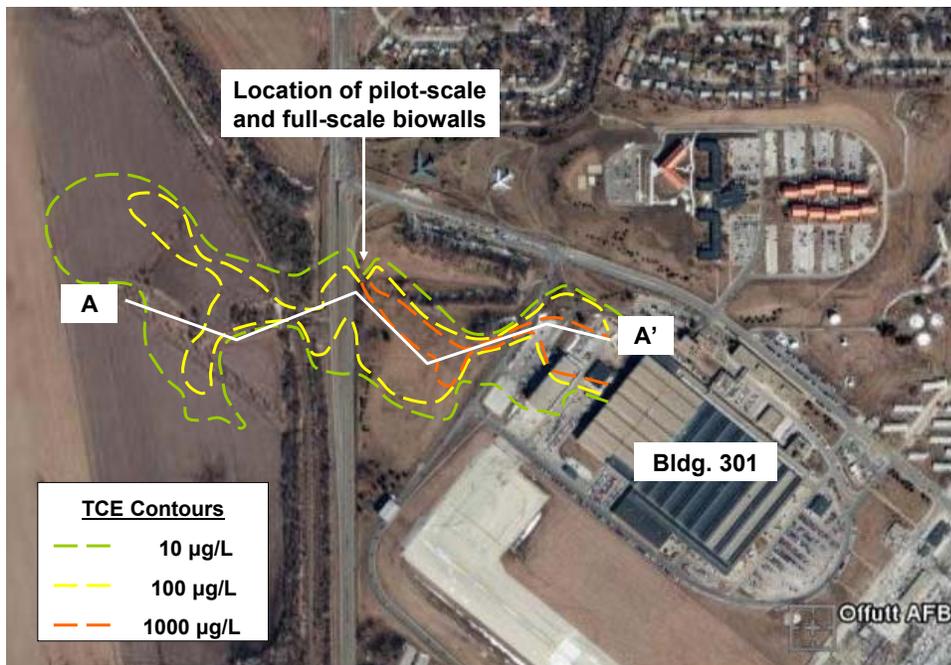


Figure 2. Location of TCE plume emanating from Building 301, Offutt AFB.

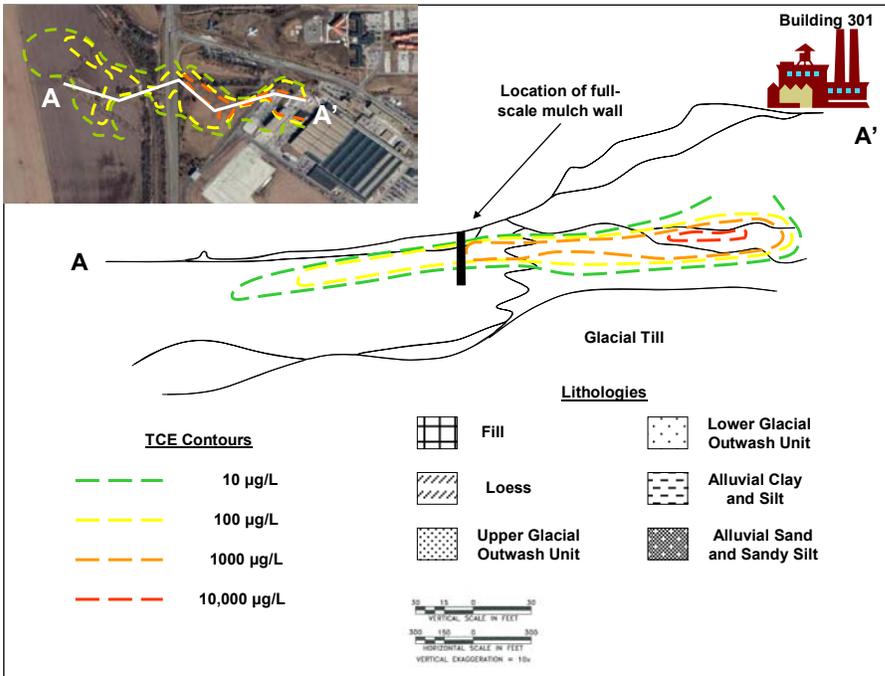


Figure 3. Cross section AA' illustrating the lithologies underlying the site.

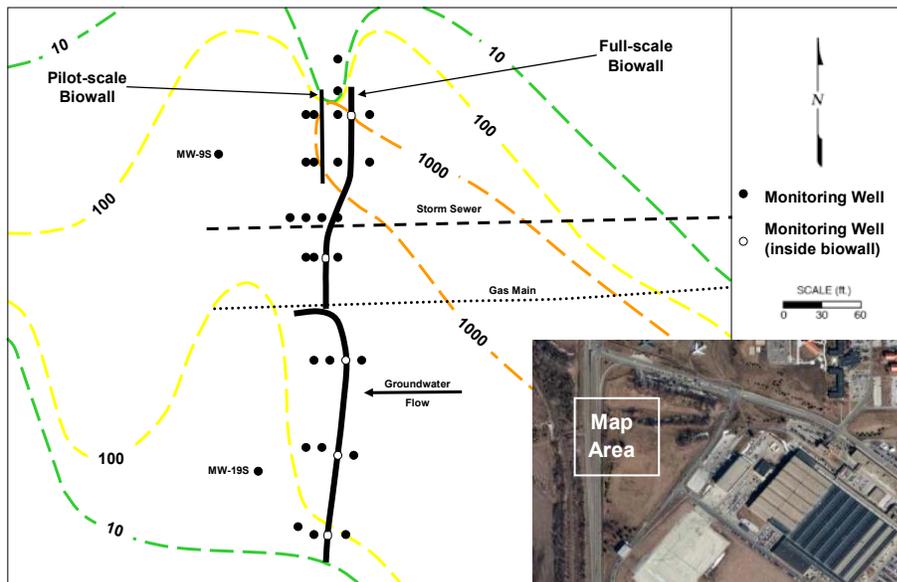


Figure 4. Locations of pilot- and full-scale biowalls and TCE isopleths at Building 301. Isopleths are labeled with TCE concentrations in µg/L obtained in spring 2000.

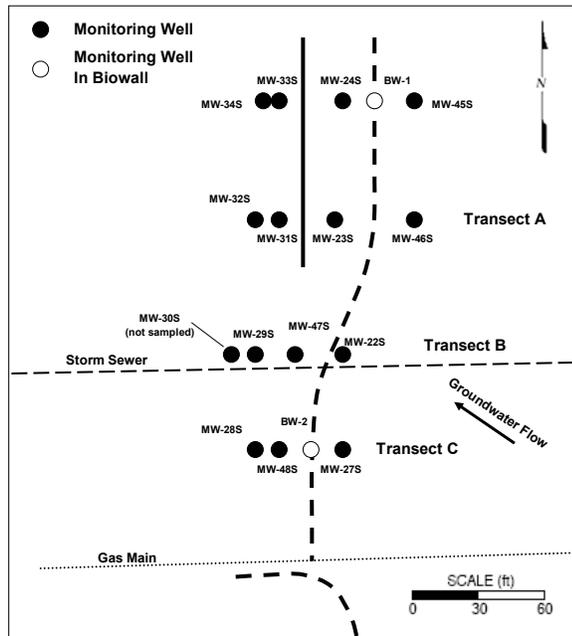


Figure 5. Location of monitoring wells in transects A, B, and C for pilot-scale and the northern portion of the full-scale biowall.

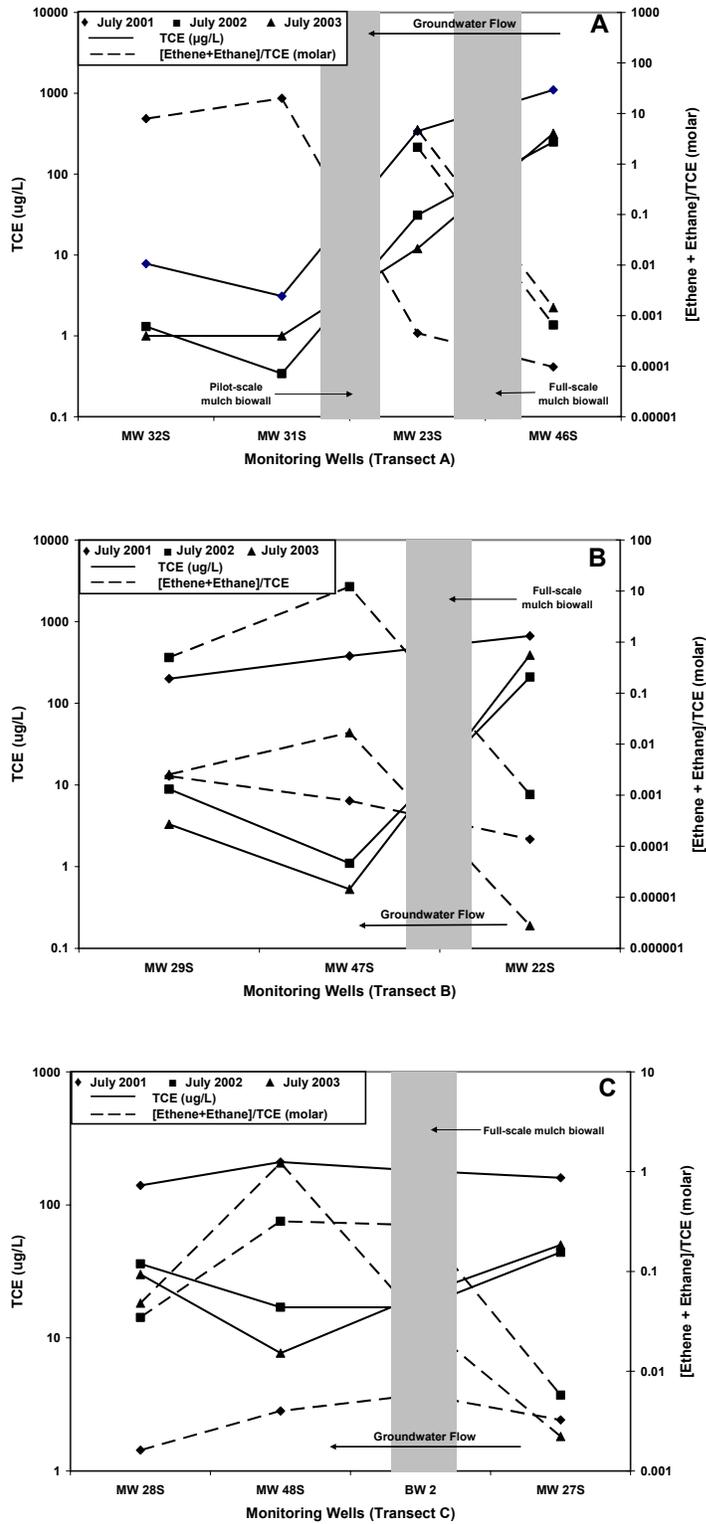


Figure 6. Changes in TCE concentrations and the molar ratio of ethene + ethane to TCE in transects A, B, and C as groundwater passes through the biowalls.

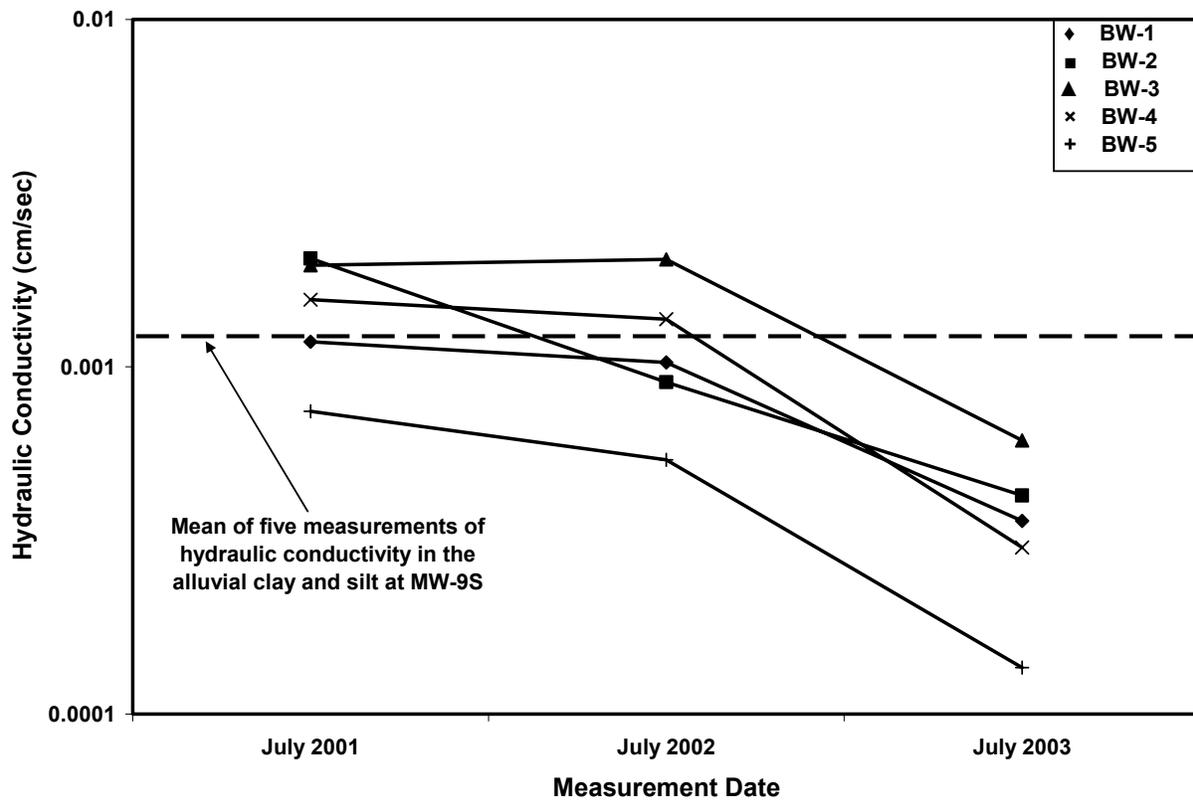


Figure 7. Observed change in hydraulic conductivity of the mulch-sand medium in the full-scale biowall from July 2001 to July 2003 at five borehole locations.

5.0 CONSTRUCTED WETLAND AT THE ABERDEEN PROVING GROUND, MD

Introduction:

The final case study in this report is an outgrowth of observations made by Michelle Lorah and her colleagues at the U.S. Geological Survey (USGS) within a natural wetland environment at Aberdeen Proving Ground, MD. They observed that a contaminant plume containing a variety of cVOC contaminants was discharging through the wetland sediments into a river. Biodegradation reactions occurring in the anaerobic wetland sediments were observed to completely decontaminate the plume. Elsewhere at the Aberdeen site contaminated groundwater was observed to upwell in springs through the bottom of the near shore environment. The nature and rate of the upwelling was such that little degradation of contaminants occurred before discharge into the surface water body. The following case study describes the development and performance monitoring of an engineered treatment system (patterned after the natural wetland: organic rich sediment seeded with appropriate anaerobic microbes) in the form of a reactive mat that was constructed over one of the springs.

Wetland Enhancement-Reactive Mat at the Aberdeen Proving Ground- West Bank Canal Creek

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INTRODUCTION

Many RCRA/CERCLA sites are located within half mile of surface water bodies in the U.S. (Tomassoni, 2000) where there is the potential for the discharge of VOCs to surface waters and associated wetlands. Several studies have demonstrated the effectiveness of natural wetlands to degrade VOCs because of wetlands inherent anaerobic/methanogenic conditions (Lorah and Olsen, 1999a, 1999b; Lorah, et al. 2001; Punshon et al., 2003; Casey, et al, 2004). The anaerobic, high carbon soil conditions in wetlands promote and sustain microbial assemblages that are known TCE degraders (Etienne et al. 2001; Lorah and Olsen, 1999a, 1999b; Lorah et al., 2001). Wetland soils also can absorb VOCs and allow longer processing times for microbial breakdown. As in upland communities, native wetland plants have been shown to phytovolatilize and phytodegrade VOCs (Punshon et al., 2003; Nzungu and Jeffers, 2001).

Laboratory and microcosm studies have enabled researchers to identify the mechanisms and processes that promote the degradation of VOCs in wetland systems. There have been a number of studies that have demonstrated the potential effectiveness of an upflow wetland system in meso-and microcosm studies (Kassenga et al. 2003; Lorah et al., 2001; Nzungu and Jeffers, 2001; Mastin et al. 2001).

Pardue et al., 2000; Pardue, 2002) provides design criteria for a constructed wetland treatment system based on the available scientific literature and draws heavily on microcosm work using simple first-order reactive transport models that account for sorption and biodegradation of VOCs. There have been a few cases of VOC treatment of groundwater using wetlands or wetland-like materials, including constructed wetlands, treatment cells, or a reactive bioaugmented mat. However, information on projects is often not readily available, poorly documented, or longterm monitoring data is not easily obtainable. Based on available information some of the better documented studies are summarized below. The best-documented of these efforts is presented here as a case study, the development by the USGS of a reactive bioaugmented mat and its deployment at the Aberdeen Proving Ground West Branch Canal Creek site initiated in 2004. While this project was only monitored for one year and therefore questions concerning sustainability are difficult to address, the technology is well documented and has the potential to be low impact as well as sustainable in sensitive wetland ecosystems.

- In Hillsdale, MI at the Schilling Farm a free surface water wetland consisting of four cells was constructed in 1998 to intercept metal cleaning solvents (Haberl et al., 2003). Groundwater is captured by a four meter deep trench and fed into the wetland cells filled with native soils and topped with muck. This wetland operated for 41 months and saw TCE levels of 1-3 ppm reduced to 150 ppb in 32 of 41 months.
- Four-acres of a giant reed (*Phragmites australis*) dominated full-scale treatment wetland was constructed at the Fort Edwards Landfill, NY to treat leachate contaminated with VOCs (DCE, VC) in 1998. This wetland is composed of three equal sized cells operating

- in parallel with a 0.5 acre polishing pond. Incoming levels were measured up to 10 ppm but have been treated to less than 10 ppb by this wetland system in 2002.
- A wetland was reconstructed along the shores of a lake in Minnesota in 2000 to intercept a groundwater plume containing TCE, DCE, and VC (Richard et al. 2001). The contaminated lake sediments were dredged and replaced with clean sand fill and planted with native wetland plugs. Performance data for this wetland other than an initial report have not been published in the literature. However, data that are available suggest that methanogenic conditions were reached in this system sufficient to degrade extant VOCs.
 - At Wright Patterson Air Force Base two vertical flow wetland pilot treatment cells were constructed in 2000 using wetland soils and wood chips to treat low concentrations of chlorinated VOCs (50 ppb PCE) (BonDurant, 2004; Clemmer, 2003). These systems are anaerobic and show much reduced levels of contaminants at the surface, often below detection limits (Shelley et al, 2002).
 - In 2004 a pilot scale test of a permeable reactive mat was constructed in a tidal wetland seep at the West Bank Canal Creek site on the Aberdeen Proving Grounds, MD. Total VOCs (31,800 µg/L were reduced by 90% by this 22 inch thick 12 X 12 ft mat composed of a mixture of crab compost, peat, and sand, and augmented with a site derived anaerobic culture.

HISTORICAL BACKGROUND

Aberdeen Proving Ground (APG) has been the site of chemical-warfare research and development since 1917. At this site chlorine, mustard gas, tear gas, phosgene, clothing impregnating material, white phosphorus, pyrotechnics, and arsenicals have been produced (Lorah et al., 1997). Large-scale production operations were greatly reduced after WWII and many of the production plants were abandoned or demolished. Chlorinated organic solvents, such as TCE, CT, TeCA (1,1,2,2-tetrachloroethane), and CF, were used as raw materials, degreasers, and for decontamination and were common in the production and filling plants. The solvents were disposed of via sewers that led to the nearby branches of Canal Creek, a freshwater tidal creek. This creek leads into the Gunpowder River and ultimately the Chesapeake Bay (figure 1). The vitrified clay sewers were constructed pre WWI and probably leaked into the groundwater. Additional groundwater contamination resulted from spills and landfills. Landfills, several of which cover the old sewer lines, contain predominantly building construction materials and debris, but may also have contained other chemical wastes (tars and sludge) and empty chemical containers. Building material from a demolished chlorine plant was also pushed into the wetland system in the 1960's. Two known sources lie within or at the wetland boundary (Phelan et al, 2002). None of the known groundwater contaminant sources have been active for 20 or more years (Lorah et al 1997).

GEOGRAPHIC SETTING

The study site is located along West Branch of Canal Creek in Edgewood County, Maryland on APG. The APG is located northeast of Baltimore, Maryland. This freshwater tidal creek is located on the Coastal Plain physiographic province of Maryland (figure 1) and flows into the Gunpowder River estuary of the Chesapeake Bay (figure 2). The tidal amplitude ranges from .5 to 2.0 ft. An estuarine emergent wetland marsh is associated with the creek drainage, although historically much of the study sites wetlands were filled. The dominant plant species in the marsh is *Phragmites australis* (common reed grass) with patches of cattails (*Typha* spp.), pickerel weed (*Pontederia* sp.), and southern wild rice (*Zizaniopsis millacea*) (Lorah et al, 1997).

HYDROLOGIC SETTING

The Canal Creek geology is characterized by thick wedge-shaped deposits of unconsolidated Coastal Plain sediments that dip to the southeast (Lorah and Clark, 1996). The Canal Creek aquifer, the main contaminated water-bearing unit, is 20-50 ft thick and is sandwiched between an uncontaminated lower confining unit (60 ft thick) and an upper confining unit in much of the upland areas. The upper confining unit is absent, however, near and within the West Branch wetland area. Within the wetland area, organic-rich wetland and stream-bottom sediments that are 6- to 25-ft thick overlie the aquifer. Wetland sediments are 10-15 ft thick in the area where the reactive mat was constructed.

The flow of water in the Canal Creek aquifer is local near the West Branch Canal Creek area, where it discharges through wetland sediments, stream bank and bottom sediments into the creek. Recharge is primarily from rainfall and occurs up gradient of the wetland systems on both sides of the creek.

NATURE AND EXTENT OF CONTAMINATION

The West Branch wetland area has been well characterized by researchers from the USGS (Lorah and Clark, 1996, Lorah and Vroblesky, 1989; Lorah et al 1997; Oliveros and Vroblesky, 1989; Olsen et al 1997; Lorah et al 2001, 2003). They have demonstrated that the natural attenuation of VOCs occurs in this wetland system and that anaerobic biodegradation is a major attenuation process (Lorah and Olsen, 1999a; Jones et al, 2004; Lorah et al 2001, 2003). The conceptual model (Figure 4) for West Branch indicates aerobic contaminated water moves from the Canal Creek aquifer and enters the organic wetland sediments of this tidal wetland system. The wetland sediments are anaerobic and provide sites for sorption onto organic matter as well as a habitat for a microbial community that can biodegrade organics such as TCE and TeCA.

While natural attenuation has been demonstrated for a major part of the wetland area, detections of VOCs in surface water indicated transport from the underlying Canal Creek aquifer does occur at some locations. Parent compounds detected included carbon tetrachloride (CT) and chloroform (CF), 1,1,2,2-tetrachloroethane (TeCA), and trichloroethene (TCE) as well as lesser amounts of some daughter compounds. Contaminant composition in the surface water was similar to that in the aquifer and led to the hypothesis that seeps were present where groundwater traveled from the aquifer to the creek with little natural attenuation.

As part of ongoing investigations, the USGS characterized the preferential groundwater discharge locations or seeps in the West Branch area (Majcher et al, 2006). This investigation utilized Thermal Infrared Imaging (TIR) from a helicopter and passive sampling methods (VOCs and methane) to identify seep areas. During the winter months active groundwater seeps have higher temperatures than the surface waters. Consistent results for TIR surveys in 3 different years determined that these seeps are discrete and spatially consistent. Two types of seeps were noted: focused and diffuse. Focused seeps are located along creek edges or branched between wetland and creek channels while the diffuse seeps are along the wetland boundary. Focused seeps were characterized by high chlorinated parent VOCs, low concentrations of VOC daughter products, and little or no methane. Diffuse seeps had higher concentrations than the focused seeps of VOC daughter compounds and detectable methane in shallow porewater samples. It is estimated that while the seeps cover less than one percent of the wetland area they contribute 20% of the total discharge of water to the wetland.

While 28 seeps were identified in the winter of 2002, seep 3-4W contained the most significant concentrations of chlorinated VOCs in the shallow groundwater investigation during 2002 and 2003. Shallow groundwater contamination in this seep is dominated by CF and CT (both detected

in excess of 10,000 µg/L), followed by TCE and PCE (maximum of both VOCs near 4,000 µg/L). Methylene chloride, 12DCE, VC, TeCA, pentachloroethane, and hexachloroethane were also detected in the seep area, although concentrations were one to two orders of magnitude lower than the other VOCs. Concentrations of the VOCs in the seep porewater generally do not decrease vertically as land surface is approached. These results differ from what was observed in earlier natural attenuation studies in the wetland area, where VOCs typically decreased to below detection levels as groundwater passes through the organic matter and is exposed to reductive dechlorination by microbes.

Analysis of available data suggest that while natural attenuation is sufficient to account for degradation of VOCs in most of the West Bank Canal Creek system the vertical discharge rate from the groundwater to the surface-water at the seeps exceeds the rate for sufficient degradation to occur. An in-situ remediation option that would treat the VOCs at the seep and minimize damage to the wetland ecosystem was sought. Two options were further evaluated in the USGS study: construction of a reactive bioaugmented mat and direct biostimulation/bioaugmentation of the existing seep area sediments. Feasibility studies were conducted to develop a culture for bioaugmentation that could be used to bioaugment the reactive mat or selected seeps and to evaluate compost/peat mixtures for the mat matrix. Seep 3-4W was selected as the site to install a pilot bioreactive mat and the subject of this case study.

DESIGN DEVELOPMENT AND CONSIDERATIONS

Culture development

Using standardized microbiological enrichment techniques, an anaerobic mixed consortium, WBC-2, were developed into a culture for bioaugmentation\biostimulation bench tests and the reactive mat pilot test in a selected seep at West Branch Canal Creek. The cultures were developed from wetland sediments and groundwater collected (upper 10 in) from the West Branch wetland area where complete anaerobic biodegradation of TeCA, TCE and their intermediate daughter products was previously shown to occur by the native microbial community (Lorah and Olsen 1999a, 1999b; Lorah et al., 2003). In a series of dilutions and transfers the consortia were developed in anaerobic cultures by feeding with TeCA, cis-12DCE, and 1,1,2-trichloroethane. Feeding the cultures with these contaminants selects only those that can feed on these contaminants and ensured that microbes involved in each step of the degradation pathway were enriched. Ultimately this enriched culture was diluted into an anaerobic culture medium of bicarbonate solution with added nutrients and trace minerals. The WBC-2 culture developed through this process was further propagated into large quantities for use in the field pilot tests by Sirem Laboratory (Guelph, Ontario).

The cultures were developed from existing native microbial strains and no genetic modification or development of new strains was performed. The developed culture WBC-2, was tested for human pathogens to ensure that no harmful microbes would inadvertently be introduced into the wetland ecosystem. Several methods were evaluated for the introduction of the developed cultures into the field. They included encapsulation into agarose or carageenan beads, freeze-drying, and direct-injection. Through the course of culture development it was noted that the consortia could tolerate up to 60 minutes of exposure to oxygen and remain viable and capable of degrading VOCs. This means that the cultures could be delivered to a remediation site by spraying without reducing their effectiveness.

Bench Tests

Through a series of batch laboratory tests the enriched culture WBC-2 was tested for survivability in different composts and with an electron donor such as lactate. In addition, because chlorinated

methanes that are potentially toxic to microbes were present in some seeps including the selected pilot test site, zero valent iron (ZVI) fillings were tested for compatibility with site sediments for incorporation in the first layer of the reactive mat. In these bench trials, ZVI effectively dechlorinated CT and CF by chemical reductive dechlorination without significant changes to porewater quality (Majcher et al, 2004).

A series of upflow column trials were conducted to (1) evaluate biodegradation by WBC-2 consortium and abiotic degradation in flow through columns, (2) evaluate redox conditions in the reactive mat matrix columns and select a commercially available material to serve as an electron donor, and (3) estimate the overall VOC mass removal for different reactive mat thicknesses. One set of duplicate columns was prepared with a mixture of compost/peat/sand; a second duplicate set was prepared with a layer of ZVI mixed with the same compost/peat/sand and overlain with a layer of compost/peat/sand without the ZVI. Initial microcosm and column experiments were conducted with compost provided by BionSoil. However, by the end of the experiments this supplier had gone out of business so five additional commercial composts were evaluated in batch microcosms to select the compost for the field test (Table 1).

Columns were constructed of Teflon that measured 30 in long by 2 in diameter. All columns were bioaugmented with the WBC-2 culture. The columns were sampled over eight months from ports located at 0, 9, 18, and 30 inches. VOCs, redox, and dissolved gases were used to estimate the rate of removal of contaminants and evaluate redox conditions. Because methane levels initially were lower than that observed in the field, sodium lactate was added to the columns as a soluble electron donor and this addition resulted in increased methane throughout the columns. A series of VOCs were run through the column including TeCA, PCE, TCE, CT, and CF to simulate field conditions at seep 3-4W.

Results of the column trials indicated that in both column types, organic compost and organic compost with ZVI, that the degradation of TeCA, PCE, and TCE was equally efficient throughout the column and only transient accumulation of daughter products occurred. The presence of CT and CF did not halt degradation of VOCs in the bioaugmented sediment, and the CT and CF was degraded in the columns without the ZVI, as well as in the column containing ZVI. Although the column tests showed that ZVI was not necessary to degrade high concentrations of the mixed VOCs present at the seep site, a layer of compost/ZVI was included in the final reactive mat design to be conservative. Sodium lactate did increase the rate of dechlorination. Chitin was also examined in noncolumn studies and was selected over the sodium lactate because of its longevity as an electron donor source. Based on analysis by BioChlor modeling program (modified) the removal of ethenes and ethanes is predicted to be near 90% for a thickness of 1-2 ft and it was estimated that 50% of chlorinated methanes would be removed with a 1.5-2 ft thickness.

In addition to the column studies, the composts and native sediments were assessed for metals content and stability, nutrient content, and presence of pathogens per EPA and Maryland regulations for composts. Fate and transport of metals was assessed using sequential extraction procedures and indicated that arsenic, lead, mercury, nickel, and zinc and are bound by the organic, carbonate, noncrystalline, and metal hydroxide fractions. A silt fence was installed to control erosion and transport to the nearby stream at the pilot site during mat construction. The Leafgro and Chesapeake Blue composts had metal levels lower than the other tested composts and the native sediments. Because it was difficult to predict the behavior of nutrients, they were monitored regularly throughout the study to evaluate their impacts on water quality. The two selected composts based on metals performance were Leafgro and Chesapeake Blue. They were tested under the Maryland Regulations for compost and were found to be in compliance for fecal coliform and salmonella acceptable levels. Chesapeake Blue was selected as the compost for the pilot scale reactive reactive mat.

Hydraulic Considerations

Various methods were used to estimate hydraulic conductivity of seep wetland sediments including Darcy's Law, cone penetrometer dissipation tests, and particle size analysis. Seepage flux (or specific discharge) also was estimated from seepage meter measurements in the seep areas. A rate of 2.5 ft/yr was estimated in previous studies for vertical gradient diffuse flow in non-seep areas in the West Bank Canal Creek wetland system (Lorah et al, 1997), whereas flow rates were one to two orders of magnitude higher in the seeps. Field and laboratory measurements were used to determine the expected hydraulic properties for the pilot reactive mat. It was estimated that for a 2 ft thick mat, with an effective porosity of 0.4-0.6, and a hydraulic gradient of 0.3 that the hydraulic residence time for the reactive mat would be 8-14 days.

ENHANCEMENT

As a remediation option a pilot test of the newly developed permeable, reactive mat was placed horizontally on the seep surface at seep 3-4W to provide a zone of enhanced degradation for VOCs in the upward-flowing groundwater before the contaminants reach the surface water. This seep was identified as one of the greatest contributors to surface-water contamination from the contaminated groundwater. The mat is 12 X 12 ft and is approximately 2 ft thick. It is composed of porous geotextile on the bottom, followed by two layers of a mixture of peat, compost, and sand, and capped with pea gravel (Figure 2). Zero valent iron was added to the organic compost/peat/sand mixture to ensure removal of the high chlorinated methanes at this seep. The upper compost/peat layer of the mat was inoculated with the WBC-2 microbial consortium; chitin also was added to act as an additional long-term substrate for the WBC-2 culture (Figure 3). An irrigation layer was built between the two compost/peat layers to provide a method for future addition of the WBC-2 culture or substrate, but use of the irrigation system has not been needed to date.

Mat construction

The reactive mat was constructed on October 5-7, 2004. Permanent floating docks and temporary aluminum walkways were established around the mat construction site at seep 3-4W (Figures 2 and 3). While erosion control silt fences were not required due to the small size of the project, they were established as a fail safe. The mat site was temporarily walled off with wooden boards and excavated to a depth of one ft below wetland grade with a vacuum pump truck. The first layer, the woven geotextile mat was put down and anchored. The reactive mat materials were mixed near the jobsite at an upland location. Using wheel barrows, layers of materials were transported over the walkways and floating docks and hand shoveled into the reactive mat. On top of the base, woven geotextile, the first reactive zone was applied: approximately 10 in thick ZVI-organic zone composed of crab compost/peat/sand mixture. This first layer was covered by the delivery system sandwiched between two layers of nonwoven geotextile. On top of this middle layer, a second reactive layer of compost/peat/sand mixture was added. WBC-2 culture was added to the top organic reactive zone during construction by direct spray application. A layer of pea gravel covered the top of the reactive mat to keep fine particles from being blown away by wind. The final constructed permeable mat was 22 in thick and extended above the original land surface to allow for settling and compaction over time.

Monitoring

An intensive sampling program was developed to monitor environmental conditions below, in, and around the permeable reactive mat. The objectives of this monitoring program was to (1)

determine mat stability, (2) demonstrate a reduction of contaminant mass flux of VOCs to surface water from the mat and estimate the efficiency of this removal with season, and (3) demonstrate the compatibility of the mat with the native wetland groundwater and surface water environments. The monitoring program established a baseline before the mat was installed and then followed its progress for 12 months after installation. A detailed description of the monitoring program can be found in Phelan and Majcher (2004).

Mat stability

Settlement of the reactive mat was assessed from a fixed wire/beam suspended over the mat. Photographs were also taken monthly to document changes in vegetation or other features. Hydraulic measurements were made before mat installation to establish base flow conditions. These measurements continued after mat installation and were collected at monthly intervals and included: seepage rates (5 seepage meters), water levels (pressure transducers in piezometers), and sediment temperatures (located in piezometers and in surficial sediments along perimeter of mat).

Mass flux measurements

VOCs and other indicators of microbial activity (redox sensitive constituents of ammonia, ferrous iron, sulfide, and methane, volatile fatty acids, hydrogen, and the composition, relative diversity, and size of the microbial community) were analyzed.

Groundwater monitoring below the mat

Deep groundwater samples from the wetland sediments beneath the mat were obtained from five Solinst model 403 continuous multi-channel tubing (CMT) piezometers that were installed under the mat before its construction. The CMTs are screened at 3, 5, 7, and 11 ft below land surface, and were labeled as "PTC" samplers. Additional groundwater samples were collected from immediately under the mat using small screens with 0.25 in diameter, air diffusing stones encased inside a sand pack by polycotton fabric (developed during West Bank Canal Creek investigations by USGS) that were set 3-4 in below the surface of the excavated wetland surface during mat construction (labeled PTN samplers). Tubing from PTC and PTN samplers were routed horizontally beneath the mat and to its perimeter so that no samplers penetrate the geotextiles.

Groundwater monitoring inside the mat

Groundwater within the mat initially was collected from nine fine-mesh screens attached to 0.125 in Teflon tubes. These were replaced with multilevel diffusion samplers (labeled PTB samplers) during the first round of sampling.

Groundwater monitoring outside the mat

Piezometers were installed outside of the mat to monitor groundwater for VOCs, water quality, and groundwater levels (Figure 9). Nine CMT piezometers placed around the boundary of the mat were screened at 1, 3, 5, 7, and 11 ft below land surface with the tops of the piezometers above high water levels. Individual piezometers in groups of three also were placed around the boundary of the mat for water-level measurements. One is a 0.75 in Teflon-lined stainless steel drive-point piezometer screened in the top of the aquifer. The second is a 0.75 diameter PVC drive-point piezometer screened at 3-4 ft below land surface. The third is a 2 in diameter, 0.010 in slotted PVC screened at 6 ft below land surface to monitor groundwater levels, specific conductance, and temperature with in-situ monitoring devices.

Surface-water monitoring

Surface water in West Branch Canal Creek was monitored for VOCs, water quality, and inorganics immediately downstream of the reactive mat. VOCs were collected every other hour for a 48 hr period during each groundwater sampling event by an ISCO 6100FR automatic

refrigerated VOC sampler within 20 ft of the mat. A multi-parameter probe was used to monitor dissolved oxygen, temperature, specific conductance, and pH in the creek. Water samples were collected for inorganic analysis every 2-3 hours for a 48 hr period once every other month by an automated ISCO water sampler.

RESULTS

Performance monitoring for one year successfully demonstrated the physical stability of the reactive mat, persistent methanogenesis suitable for reductive dechlorination, and a reduction in the concentrations of chlorinated solvents seeping into surface water to below or near detection levels. Data presented in Figures 5-7 are representative of levels seen at all sample points across the mat and are presented as a vertical profile with six depths at one sampling location (Table 2). The PTB data are from diffusion samplers located in the upper bioaugmented layer of the mat; PTN represents data from samplers located 3-4 in immediately below the woven geotextile base of the mat; and the PTC data are from the multilevel piezometers screened at various depths in the wetland sediments beneath the mat. Methanogenic conditions were generated in the reactive mat and were sustained throughout the monitoring period November 2004-October 2005. Elevated levels of methane were seen at the PTB sampling points (Figure 5) as was hydrogen (not shown). These levels were optimal for the efficient reductive dechlorination by the WBC-2 culture. These conditions were not observed in the groundwater immediately below the reactive mat.

The first graph in the Figure 6 series shows baseline conditions before the mat was installed and includes peeper porewater data for the top 1 ft of wetland sediment that was removed during mat construction. In the baseline at seep 3-4W, elevated levels of the VOCs, PCE, TCE, CF, and CT were noted at the seep surface or near surface. Also detected in the groundwater, were DCE, TeCA, pentachloroethane (PCA), hexachloroethane (HCA), and methylene chloride (MeCl) at low levels. The mat functioned to degrade VOCs immediately. The first sampling event after construction (November, 2004) showed a reduction in VOCs in the mat and at the base of the mat (Figure 6). High levels of TCE, PCE, CF, and MeCl were greatly reduced or not detected in the PTB level samplers. Subsequent sampling events in March and September 2005 showed similar trends. There appeared to be some reduction in the mat degradation rates in the March, 2005 that may be due to an inhibition of the microbial community with the colder winter months. However, with the onset of warmer temperatures the levels of total VOCs (Figure 7) and specifically levels of TCE, PCE, CF, and CT were reduced to near nondetect levels (Figure 6). This pattern suggests that the microbial community recovered with the warmer spring and summer temperatures. Similar patterns and results were corroborated by laboratory batch tests performed with sediments collected from the mat to confirm the continued activity of WBC-2.

Production of ethene and ethane, which are reductive dechlorination end products of the chlorinated ethene and chlorinated ethane parent contaminants (TeCA, HCA, PCA, PCE, TCE), was detected in the mat (Figure 8). There was no apparent stalling of the reductive dechlorination process at the daughter products DCE (Figure 6) or vinyl chloride (levels were lower than those for DCE and are not shown on figures).

Surface-water monitoring showed no increase in VOCs over baseline. In addition other measured constituents such as phosphate remained comparable with baseline measurements, indicating that mat construction did not affect surface water quality.

Post mat construction water levels did not change from those measured before installation, indicating that the permeable reactive mat did not alter hydraulic conditions and that flow did not bypass the mat. In addition, thermal infrared imaging performed in February 2005 did not locate any new seeps that might have been generated as a result of mat construction and subsequent alteration of groundwater flow.

Using BioChlor and making assumptions about uniform porosity, and normalizing across horizontal planes below and within the mat, mass removal for VOCs was estimated. Mass removal of total chlorinated ethenes and ethanes was greatest in November, 2004 at 95% and decreased to 90% following the winter months. Mass removal of chloromethanes (CT, CF, and MeCl) reached 95% in the upper organic layer of the mat in November 2004, and dropped to 81% in March, 2005. Mass removal was between 96 and 99 percent for all VOCs in June and September 2005. This data and other suggest a seasonal trend with the highest removal rates in the fall and summer months and slightly lower removal rates in the winter.

As a result of this work by USGS a Cooperative Research and Development Agreement has been formed with GeoSyntec Consultants toward additional development and testing of the WBC-2 culture and reactive mat.

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Table 1. Tested composts and mixtures in microcosm and upflow column studies.

Seep sediment

compost/peat/sand mixture

ZVI/organic mixture with overlying organic mixture

Paygro dairywaste-derived

TLC dairywaste-derived

Chesapeake Green poultry waste-derived

Leafgro leaf compost

Chesapeake Blue crab compost

Table 2. Vertical profile depth (ft) for groundwater samples presented in figures 5-8.

Sample point	Depth below land surface (ft)	Location relative to mat
PTB7 B	-0.5	In mat
PTB7C	-0.17	In mat
PTN7-1	1	Directly below mat
PTC4A-1	5	Wetland porewater below mat
PTC4B-1	8	Wetland porewater below mat
PTC4C-1	11.9	Below mat at interface of wetland sediment and Canal Creek aquifer

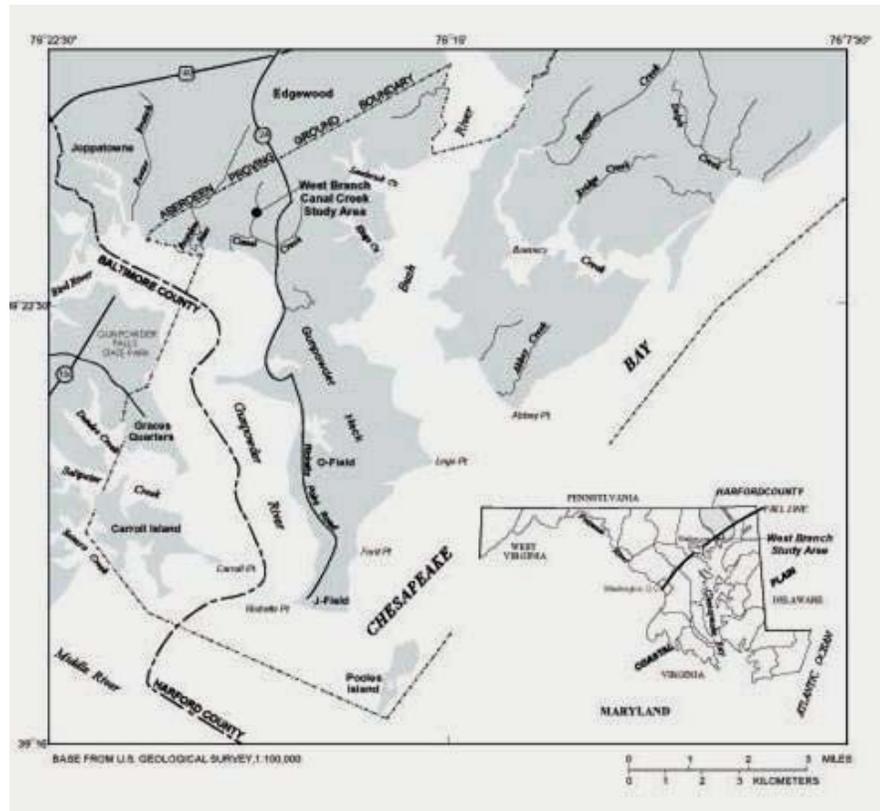


Figure 1. Location of Canal Creek area and West Branch study area, Aberdeen Proving Ground, Maryland. (Lorah et al, 1997, p. 5)

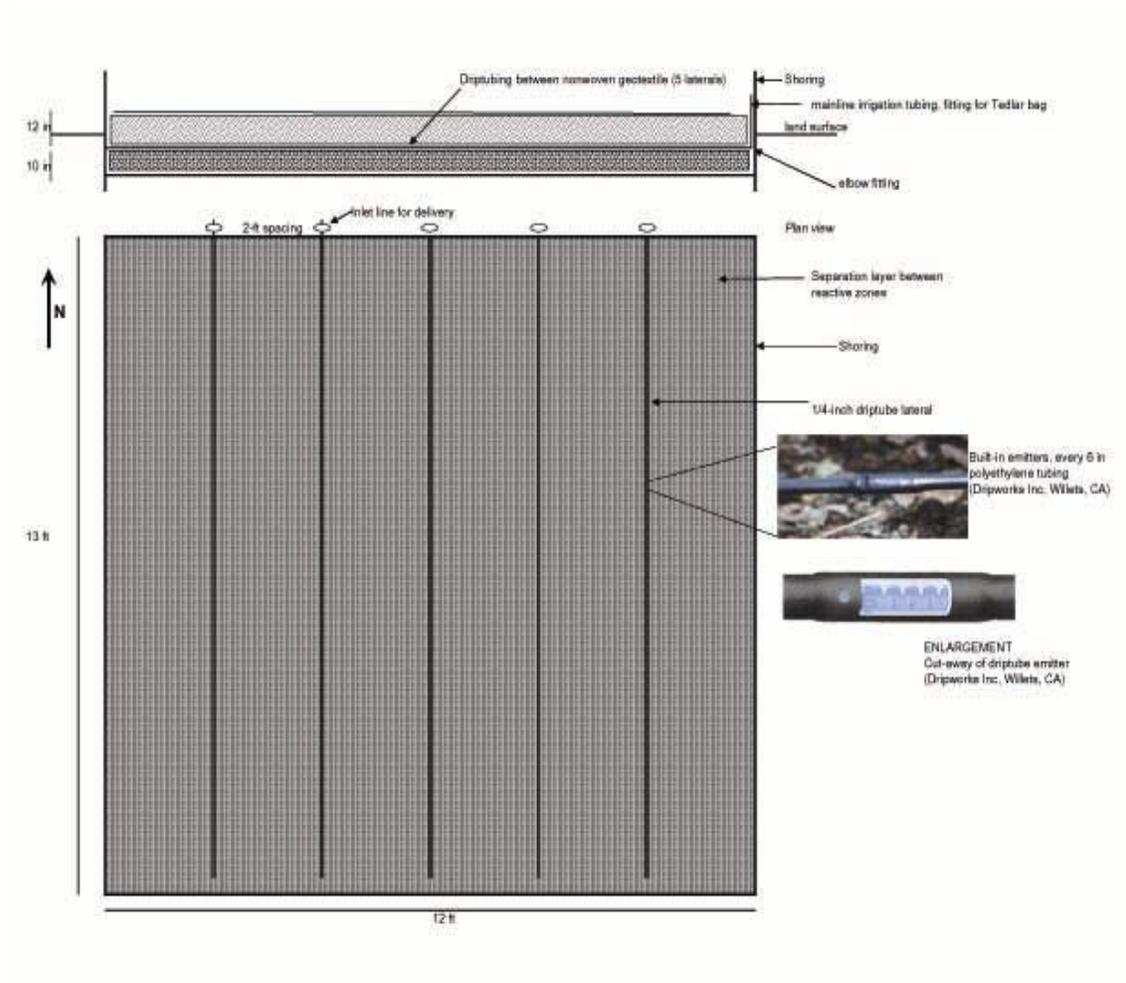


Figure 2. Reactive mat Schematic for seep 3-4W, West Branch Canal Creek. (Majcher et al, 2004).



Figure 3. Spraying WBC-2 culture into organic layer at reactive mat during construction, October 2004. (Photograph courtesy of Michelle Lorah, USGS).

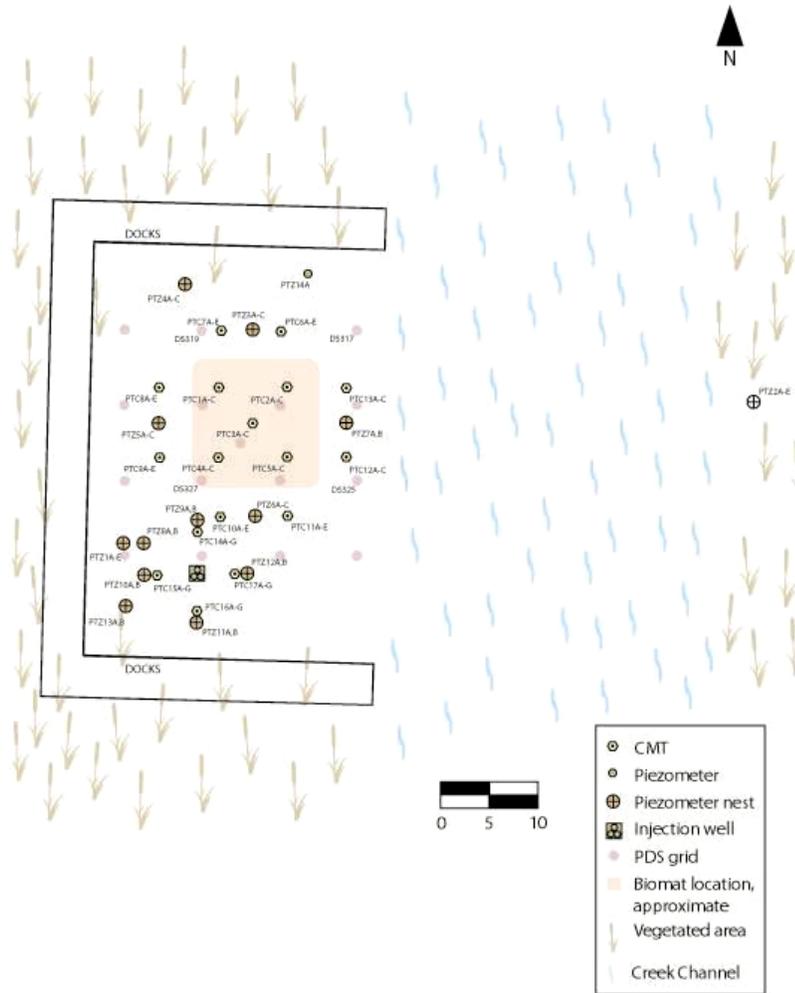


Figure 4. Seep 3-4 Pilot Test Sampling Device Locations. (Majcher et al, 2004)

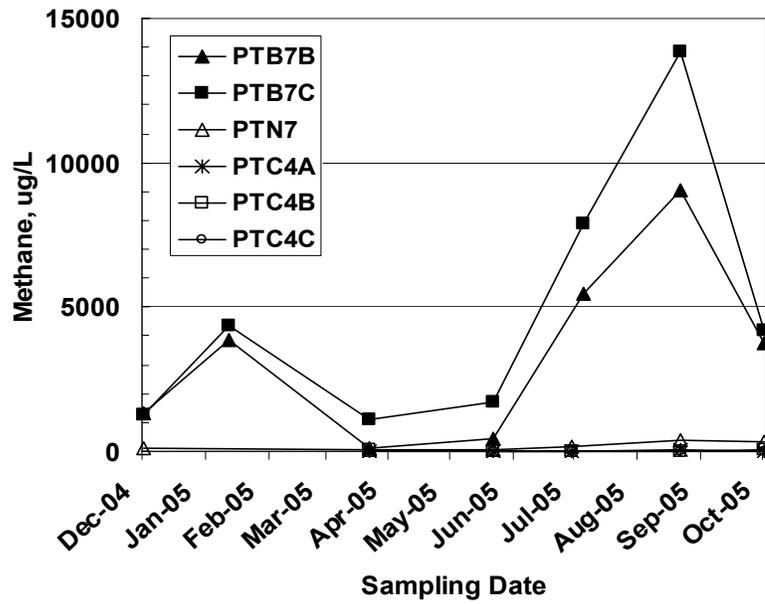


Figure 5. Levels of methane at reactive mat December 2004 to October 2005. See Table 2 for sample depths.

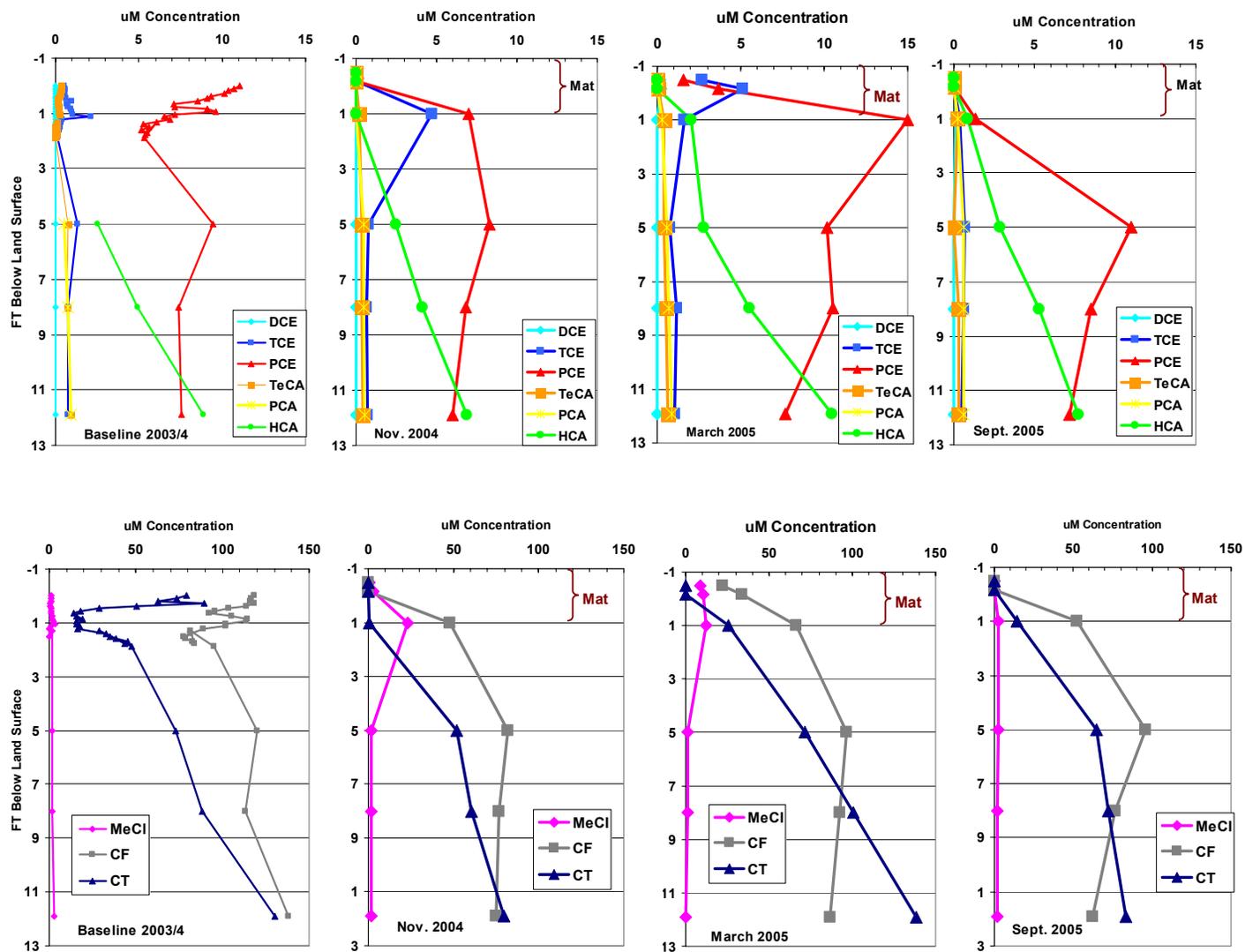


Figure 6. Vertical profiles of VOCs at one location in the reactive mat (samplers PTB7, PTN7, and PTC4). Shown are baseline samples and sampling events during November 2004, March 2005, and September 2005. See Table 2 for sample depths.

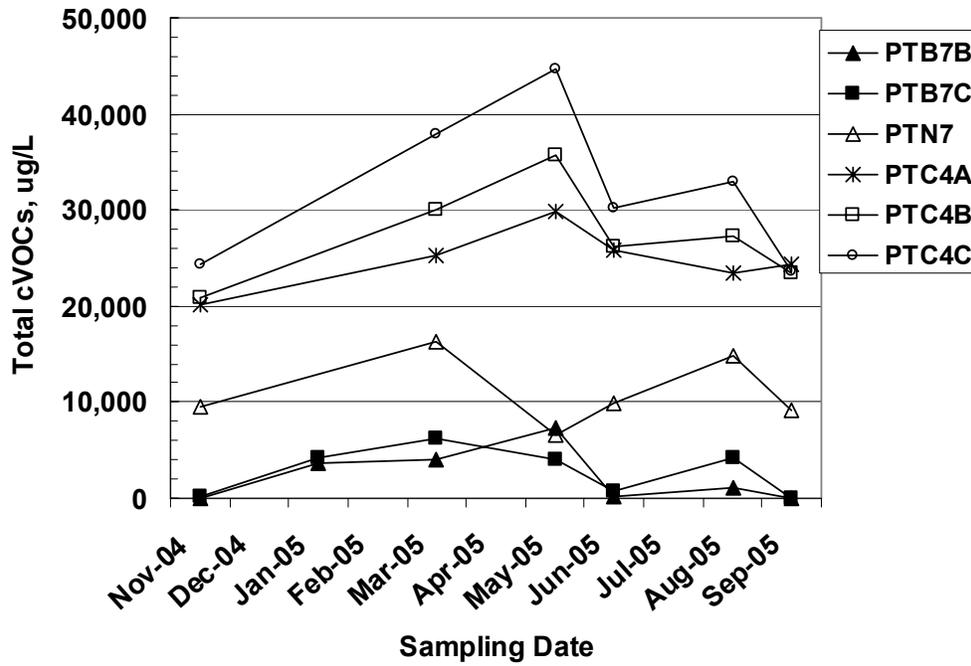


Figure 7. Levels of total VOCs at the reactive mat December 2004 to October 2005. See Table 2 for sample depths.

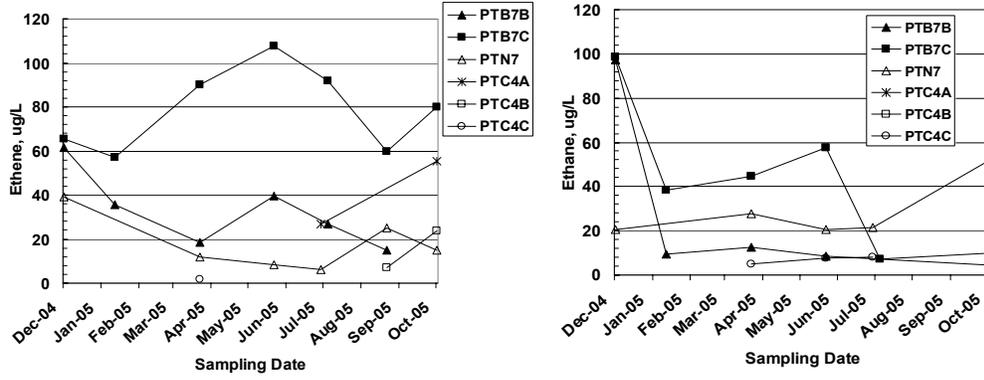


Figure 8. Ethene and Ethane levels at the reactive mat from December 2004 to October 2005. See Table 2 for sample depths.